

Effect of Glycol and Resorcinol in Inhibition of Sulphur Dioxide Autoxidation in Atmosphere

Manoj Kumar

Lecturer in Chemistry, Government PG College, Kota, Rajasthan, India

ABSTRACT: Resorcinol is a very white crystalline solid that becomes pink on exposure to light if not completely pure. Burns although ignition is difficult. Density approximately 1.28 g / cm³. Irritating to skin and eyes. Toxic by skin absorption. Used to make plastics and pharmaceuticals. Resorcinol is a benzenediol that is benzene dihydroxylated at positions 1 and 3. It has a role as an erythropoietin inhibitor and a sensitiser. It is a benzenediol and a member of resorcinols. Resorcinol is a 1,3-isomer (or meta-isomer) of benzenediol with the formula C₆H₄(OH)₂. It is used as an antiseptic and disinfectant in topical pharmaceutical products in the treatment of skin disorders and infections such as acne, seborrheic dermatitis, eczema, psoriasis, corns, calluses, and warts. It exerts a keratolytic activity. Resorcinol works by helping to remove hard, scaly, or roughened skin. Although it is primarily indicated for use as a topical application, resorcinol also possesses a well-documented anti-thyroidal activity that is generally not relied upon for any kind of formal therapeutic indication.

Glycols are aliphatic dihydric alcohols. Primary and secondary glycols are thick liquids, and tertiary glycols (pinacones) are crystalline solids. The principal glycols to which people are or have been exposed, either occupationally or in medicinal products. Glycol is a chemical compound that is diol containing two hydroxyl groups. In a clinical setting, most commonly encountered glycol is ethylene glycol. Other less frequently encountered glycols include diethylene glycol, propylene glycol, ethylene glycol monobutyl ether (EGBE), and ethylene glycol monomethyl ether (EGME). Glycols are associated with severe morbidity and an increased risk of death. Ethylene glycol is a colorless, odorless, and relatively nonvolatile liquid that is commonly used as an industrial chemical. It is a major ingredient of antifreeze and deicing solutions due to its high boiling point (197°C) and low freezing point. It may be accidentally ingested, particularly by children as it tastes sweet, or intentionally ingested by adults as an ethanol substitute or to inflict self-harm. Although ethylene glycol toxicity is uncommon, when it does occur, it can have a high morbidity or mortality. According to the 2016 Annual Report of the American Association of Poison Control Centers, there were 6325 single exposures to ethylene glycol with 32 fatalities. Similar to ethylene glycol, diethylene glycol is used in antifreeze, brake fluids, and deicing solutions.

KEYWORDS : autoxidation, resorcinol, glycol, medicines, effects

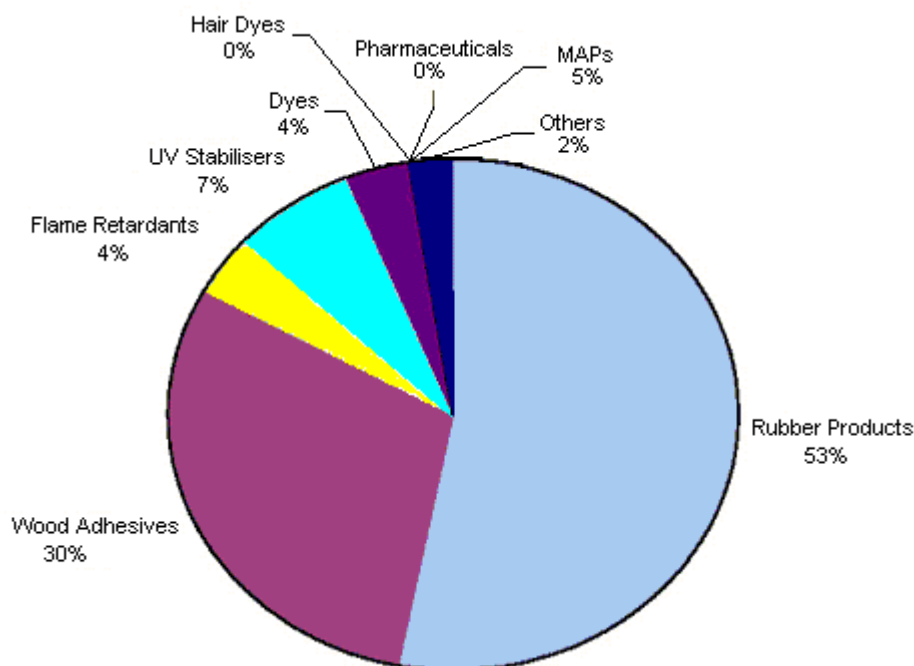
I. INTRODUCTION

This study suggests that since organic inhibitors are found in the atmosphere, their concentrations and their influence on the oxidation of aqueous SO₂ should be taken into account. The intervention of glycol and resorcinol in the autoxidation of aqueous SO₂ plays a role in deciding the fate of both glycol, resorcinol and SO₂. The influence of inhibitors may be used to calculate the lifetime of SO₂, resorcinol has high values of k_{inh} and, therefore, it would be degraded by sulfate radical anions in atmospheric waters.[1,2]

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 7, July 2016



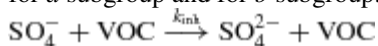
Resorcinol

The oxidation of dissolved sulfur dioxide, sulfur(IV), by oxygen proceeds through the involvement of sulfoxy radicals among which sulfate radical anion is the main chain carrier. When organics are present, they inhibit the oxidation of sulfur(IV) via scavenging of SO_4^- radicals. In contrast to previous studies, which were limited mostly to aliphatic compounds, this paper presents the results of the effect of 13 new volatile organic compounds (VOCs) including aromatic and heterocyclic on uncatalyzed sulfur(IV) autoxidation at pH 8.2 and 25°C. In all cases, the kinetics was first order in the presence and absence of VOCs and experimental rate law was :

$$-d[S(IV)]/dt = k_{obs} [S(IV)] = k_o [S(IV)] / [1 + B[Inh]]$$

where $-d[S(IV)]/dt$ is the rate of sulfur(IV) disappearance, k_{obs} is the first-order rate constant in the presence of inhibitor, k_o is the first-order rate constant in the absence of inhibitor, $[S(IV)]$ is concentration of sulfur(IV) at time, t , and B is an inhibition parameter.[3,4]

VOCs cause inhibition by scavenging sulfate radical anions, which propagate the autoxidation chain. An analysis of B values for 21 aliphatic, aromatic, acyclic, and heterocyclic organic compounds showed that these to be related for a subgroup and for b subgroup.[5,6]



a subgroup resorcinol

$$B = (0.87 \pm 0.21) \times 10^{-3} k_{inh}$$

b subgroup glycol

$$B = (1.2 \pm 0.3) \times 10^{-3} k_{inh}$$

II. OBSERVATIONS

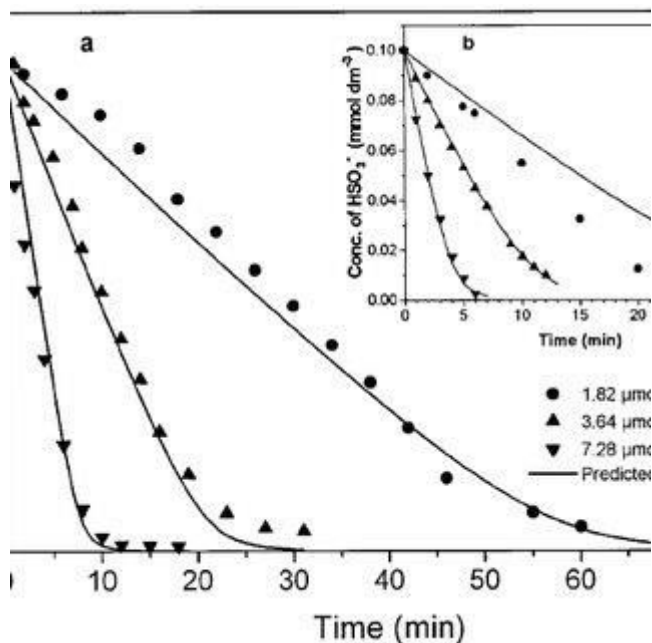
Today, acid rain problem is one of the serious global problems to the environment in which pH of the rain water decreases, causing harmful effect to nature, buildings, monuments, vegetation and human being as well. Therefore, the objective of the paper to find out some organic inhibitors present in the atmosphere that inhibited the acid rain.[7,8]

International Journal of Innovative Research in Science, Engineering and Technology

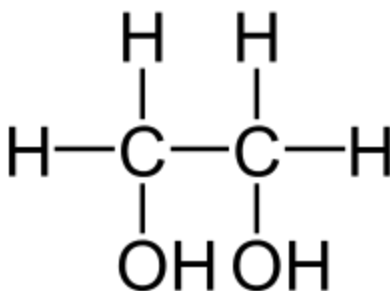
(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 7, July 2016

The thermodynamic parameters were found as frequency factor ($1.59 \times 10^{-6} \text{ s}^{-1}$), entropy ($-358.92 \text{ J K}^{-1} \text{ mol}^{-1}$), enthalpy ($20.97 \text{ k J mol}^{-1}$), and Gibbs free energy ($172.83 \text{ k J mol}^{-1}$), respectively.[9]



We observed that glycol and resorcinol acts as an inhibitor in copper catalyzed autoxidation of SO_2 in acidic medium. Therefore, on the basis of the observed results a free radical mechanism has been identified. The results are useful for modeling rain water acidity and therefore a great use of meteorology and atmospheric chemistry. This study is important in understanding the mechanism of the oxidation of S(IV) by O_2 . [10,11]



Glycol

This study suggests that since organic inhibitors are found in the atmosphere, their concentrations and their influence on the oxidation of aqueous SO_2 should be taken into account. The intervention of glycol and resorcinol in the autoxidation of aqueous SO_2 plays a role in deciding the fate of both of these and SO_2 . The influence of inhibitors may be used to calculate the lifetime of SO_2 , glycol and resorcinol has high values of k_{inh} and, therefore, it would be degraded by sulfate radical anions in atmospheric waters. [12,13]

III. DISCUSSION

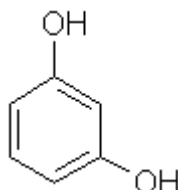
As reported before a radical mechanism operates in those reactions in which the inhibition parameter lies in the range $10^3 - 10^4$. In this study the value of inhibitor parameter is found to be $10^4 - 10^5$, which lies in above the range. These

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

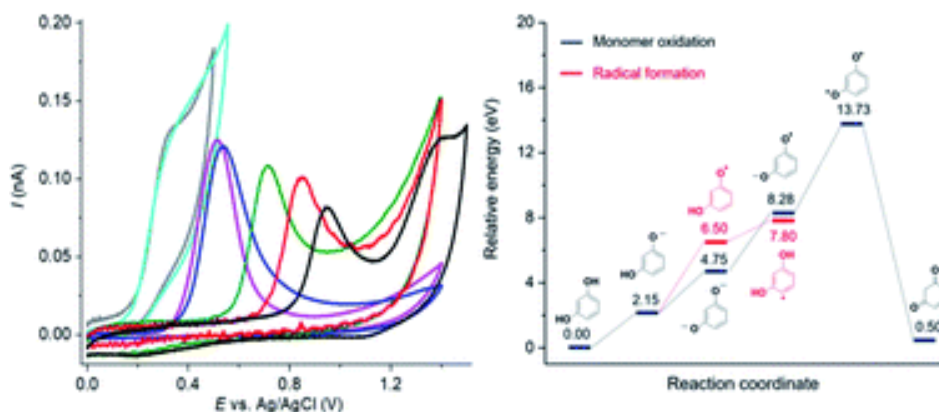
Vol. 5, Issue 7, July 2016

results strongly support the radical mechanism. In contrast the results conclusively show that glycol and resorcinol act as inhibitors for S(IV) autoxidation and the order in uncatalyzed reaction is formation of acid. [14,15]



Resorcinol

SO₂ is widely recognized as an air pollutant and is a known cause of acid rain. At a sufficiently high level, it also causes respiratory diseases. A much lesser known side of SO₂ is its endogenous nature and possible physiological roles. There is mounting evidence that SO₂ is produced during normal cellular metabolism and may possibly function as a signaling molecule in normal physiology. The latter aspect is still at the stage of being carefully examined as to the validity of classifying SO₂ as a gasotrasmmitter with endogenous signaling roles. One difficulty in studying the biological and pharmacological roles of SO₂ is the lack of adequate tools for its controllable and precise delivery. Traditional methods of using SO₂ gas or mixed sulfite salts do not meet research need for several reasons.[16,17] Therefore, there has been increasing attention on the need of developing SO₂ donors or prodrugs that can be used as tools for the elucidation of SO₂'s physiological roles, pharmacological effects, and possible mechanism(s) of action. [18]



IV. RESULTS

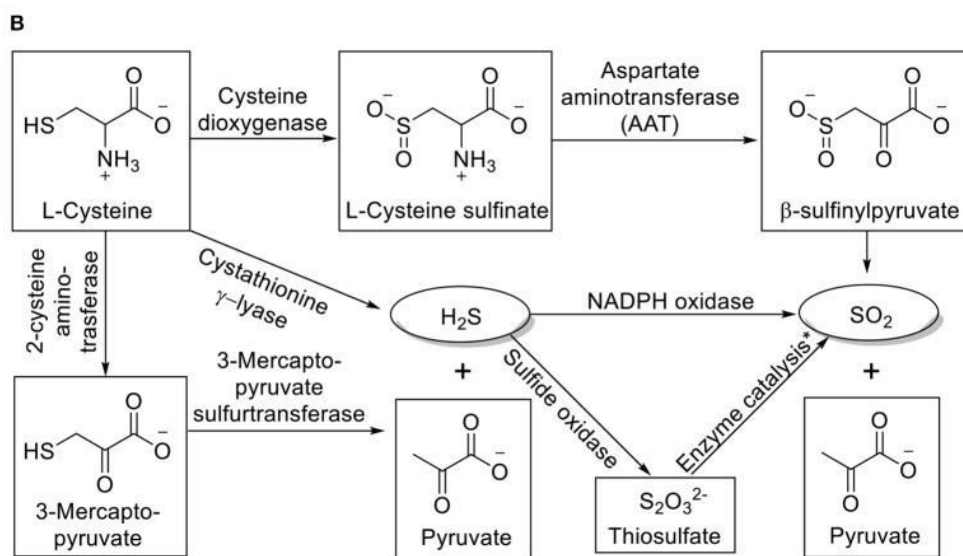
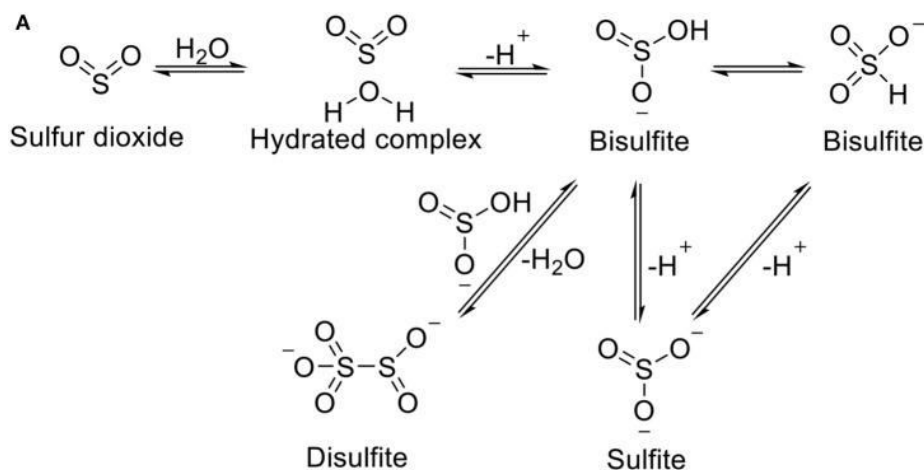
Much of the recent rise in interest for SO₂ originates from its possible roles as an endogenous signaling molecule. As a gaseous molecule, SO₂ has a Henry's constant of 1.23 mol kg⁻¹ bar⁻¹. It can readily dissolve in water and form a hydrated SO₂ complex (SO₂·H₂O), which in turn undergoes first and second dissociation to give bisulfite (HOSO₂ or HSO₃) and sulfite (SO₃²⁻) ions. The first and second pK_as of SO₂·H₂O are 1.81 and 6.97. Accordingly, it can be calculated that under physiological pH, the bisulfite and sulfite are formed in a molar ratio of about 1: 3. Dimerization of bisulfite would form disulfite (S₂O₅). Due to the abundance of water in the biological system, all the species exist in an equilibrium. Therefore, it will be hard to isolate one species out and study its sole effect; and it is important to study SO₂ and its derivatives as a whole. Besides hydration, another important aspect of SO₂ chemistry is its redox chemistry, which is much more complex in a biological setting. SO₂ and its derivatives are interconnected with many other sulfur species through enzymatic or non-enzymatic processes. Generally speaking, SO₂ is produced as an intermediate of metabolism of sulfur-containing compounds and can be oxidized further to generate other sulfur species. For example, SO₂ can be produced from L-cysteine through sequential catalysis of cysteine dioxygenase and aspartate aminotransferase (AAT); oxidation of sulfite through sulfite oxidase can produce sulfate; H₂S can be generated from L-

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 7, July 2016

cysteine by cystathionine β -synthase, and further oxidation by NADPH oxidase would generate SO_2 ; under ambient conditions, more reactive species such as SO_3 and SO_4 can be produced through autoxidation of sulfite. [19]



V. CONCLUSION

Various SO_2 donors and prodrugs have been developed and have shown greater potency for therapeutic applications compared with traditional methods of delivering SO_2 . For example, thiol-triggered prodrugs are well-adopted as two-prong antibacterial reagents; UV light-sensitive prodrugs allow for localized release of SO_2 gas to induce cell death; esterase-sensitive prodrugs deliver SO_2 into the cells with higher efficiency and specificity. Besides afore-mentioned applications, such SO_2 donors and prodrugs may as well serve as tools for exploring the mechanism of SO_2 's biological functions. SO_2 prodrugs with varied release rates would allow studies of SO_2 's biological effect in greater detail and suit personalized prescription requirement in potential therapeutic applications. Triggered release mechanism should improve the delivery efficiency of SO_2 to target cells/tissues/organs, and lower required dosage to achieve desired effect. Controllable release of SO_2 should facilitate studies on the crosstalk of SO_2 with other gasotransmitters and drugs in a defined manner. Nevertheless, the current prodrugs suffer more or less from problems such as low release

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 7, July 2016

efficiency, low drug loading efficiency, and poor water solubility. As medicinal chemists are most concerned with, the chemical properties of these prodrugs should be optimized to allow good pharmacokinetics performance. Moreover, the components/byproducts of the prodrug system should also be taken into consideration to minimize complications of SO₂'s effect as well as side effects on the biological system. Future research in this area should better address these problems. Possible approaches could be using chemical modifications and drug delivery systems to improve the properties of current prodrugs. According to the reported biological and pathological roles of SO₂, it is also important to develop SO₂ donors with easily-modified tissue specificity (e.g., cardiovascular system specificity). Therefore, developing biomarker-conjugated SO₂ prodrug systems should be of great biological and therapeutic interests to researchers in this area.[20]

REFERENCES

- [1]. Sharma, A.K. Sharma, R. and Prasad, D.S.N., (2017). Acid rain chemistry, Catalysis and Inhibition of SO₂ in environment" ISBN 978-3-659-91204-7" LAP Lambert Academic Publishing Germany.
- [2]. Gupta, K.S., Jain, U., Singh, A., Mehta, R.K., Manoj, S.V., Prasad, D.S.N., Sharma, A., Parashar, P., Bansal, S.P., (2004). Kinetics and mechanism of the osmium (VIII)-catalysed autoxidation of aqueous sulfur dioxide in acidic and alkaline media. *J. Indian Chem. Soc.*, 81: 1083-1092.
- [3]. Mudgal, P.K., Sharma, A., Mishra, C.D., Bansal, S.P., Gupta, K.S. (2008). Kinetics of ammonia and ammonium ion inhibition of the atmospheric oxidation of aqueous sulfur dioxide by oxygen. *J. Atmos. Chem.*, 61: 31-55.
- [4]. Sharma, A.K., Prasad, D.S.N., Sharma, R., (2018). Catalysis and Inhibition of SO₂ in Atmospheric Environment- A perspective of acid rain chemistry "ISBN978-93-86841-59-9" chapter published in book entitled Analytical techniques in Chemical and biological sciences Discovery publishing house Pvt. Ltd New Delhi India.
- [5]. Sharma, A.K., Acharya, S., Sharma, R., Saxena, M., (2012). Recovery and Reuse of SO₂ from Thermal Power Plant Emission(Chapter), in Book entitled Air Pollution - Monitoring, Modelling, Health and Control, Dr. MukeshKhare (Ed.), ISBN: 978-953-51-0381-3, DOI: 10.5772/32390. InTech OPEN ACCESS PUBLISHER, University campus Croatia.
- [6]. Prasad, D.S.N., Mehta, R.K., Parashar, P., Madnawat, P.V.S., Rani, A., Singh, U., Manoj, S.V., Bansal, S.P., Gupta, K.S., (2003). Kinetics of surface-catalysed autoxidation of aqueous sulfur dioxide in cobalt (III) oxide suspensions. *J. Indian Chem. Soc.*, 80: 391-394.
- [7]. Bhargava, R., Prasad, D.S.N., Rani, A., Bhargava, P., Jain, U., & Gupta, K.S. (1993). Kinetics of autoxidation of aqueous sulphur dioxide in suspensions of nickel (III) oxide. *Transit. Metal Chem.*, 17: 238-241.
- [8]. Prasad, D.S.N., Rani, A. & Gupta, K.S. (1992). Surfacecatalyzed oxidation of S (IV) in aqueous silica and copper (II) oxide suspensions. *Environ. Sci. Technol.*, 26: 1361-1368.
- [9]. Gupta, K.S., Singh, R., Saxena, D., Manoj, S.V. & Sharma, M., (1999). Role of manganese dioxide in the autoxidation of sulfur (IV) in oxic and anoxic suspensions *Ind. J. Chem.*, 38A: 1129-1138.
- [10]. Manoj, S.V., Mishra, C.D., Sharma, M., Rani, A., Jain, R., Bansal, S.P. & Gupta, K.S., (2000). Iron, manganese and copper concentrations in wet precipitations and kinetics of the oxidation of SO₂ in rain water at two urban sites, Jaipur and Kota, in western India. *Atmos. Environ.*, 34: 4479-4486.
- [11]. Ghosh, M. K., & Rajput, S.K. (2012). Kinetics and Mechanism of Lanthanum (III) Catalysed Oxidation of Dgalactose by Cerium (IV) in Aqueous Acidic Medium, *J Applicable Chem.*, 1(4): 541-550.
- [12]. Meena, V., Dayal, Y., Saxena, D., Rani, A., Chandel, C.P. & Gupta, K.S., (2016). The influence of diesel—truck exhaust particles on the kinetics of the atmospheric oxidation of dissolved sulfur dioxide by oxygen. *Environ Sci Pollut Res.*, 23(17): 17380-92.
- [13]. Meena, V., Dayal, Y., Rathore, D.S., Chandel, C.P. & Gupta, K.S., (2017). Inhibition of Aqueated Sulfur Dioxide Autoxidation by Aliphatic, Acyclic, Aromatic, and Heterocyclic Volatile Organic Compounds *Int. J. Chem. Kine.*, 49(4): 221- 233.
- [14]. Meena, V., Dayal, Y., Rathore, D.S., Chandel, C.P. & Gupta, K.S., (2017). Inhibition of atmospheric aqueous phase autoxidation of sulphur dioxide by volatile organic compounds: mono-diantri-substituted benzenes and benzoic acids *Prog. React Kinet and Mech.*, 42(2): 111–125.
- [15]. Wilkosz, I. & Mainka, A., (2008). Mn (II)-catalysed S(IV) oxidation and its inhibition by acetic acid in acidic aqueous solutions. *J. Atmos. Chem.*, 60: 1-17.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 7, July 2016

- [16]. Ziajka, P. & Pasiuk-Bronikowska, W. (2003). Autoxidation of sulfur dioxide in the presence of alcohols under conditions related to tropospheric aqueous phase, *Atmos. Environ*, 37: 3913-3922.
- [17]. Podkrajsek, B., Grgic, I., Tursic, J. & Bercic, G., (2006). Influence of atmospheric carboxylic acids on catalytic oxidation of sulfur (IV). *J Atmos. Chem.*, 54:103-120.
- [18]. Gupta, K.S. (2012). Aqueous phase atmospheric oxidation of sulfur dioxide by oxygen: role of trace atmospheric constituents metals, volatile organic compounds and ammonia. *J. Indian Chem. Soc.*, 89: 713-724.
- [19]. Sharma, A.K., Sharma, R., Prasad, D.S.N., Parashar, P. & Gupta, A.K. (2015). Formic Acid inhibited Ag (I) Catalysed Autoxidation of S(IV) in Acidic Medium, *J. Chem. Chem. Sci.*, 5(12): 760-771.
- [20]. Sharma, A.K., Sharma, R., Prasad, D.S.N., Parashar, P. & Gupta, A.K. (2016). Ag (I) catalysed autoxidation of S (IV) and its inhibition by isopropyl alcohol in acidic medium. *Chem. Sci. Rev. Lett.*, 17(5): 14-23.