



Dynamic of Atmospheric acid precipitation –Reactions in aqueous phase (A review study)

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ABSTRACT

This review article is from the dissertation of Dr DSN Prasad submitted for their MPhil. This is an extensive study of pollutants like SO_2 , NO_2 and suspended particulate matter (SPM) in different cities of India. India as a whole adds about 7 million tonnes of particulates and 4 million tonnes of SO_2 per annum to the atmosphere. Different properties of SO_2 have been given in this dissertation in chapter II. We know H_2SO_4 is produced by hydrolysis of SO_2 in contact process.

I. INTRODUCTION

Man's ever increasing needs and search for comforts have led to a rapid industrialization and to an explosion of automobiles. As a consequence a large number of harmful chemicals are being continuously released to the atmosphere giving rise to several chemical pollution phenomena such as green house effect, arctic haze, photochemical smog acid rain and a recently confirmed phenomenon of ozone hole. Of these acid rain is most wide spread and has engulfed a major part of Northern Hemisphere. A recent UNEP/WHO Study (1988) has shown that about two thirds of world's 1.8 million city dwellers breathe air that contain disturbingly high levels of sulphur dioxide and dust.

Acid rain is a phenomena of common occurrence in northeastern US, South eastern Canada, several Atlantic and European countries. The instances of acid rain/snow fall are known in Japan, China, USSR, Chile, Brazil, Point Barrow (North Pole) and even Alaska. In our own country the level of SO_2 in atmospheric environment is increasing and therefore the danger of acid rain cannot be simply wished away. The environmentalists are particularly worried about the possible damage to Taj Mahal due to close proximity of Mathura refinery and presence of several foundries in the city of Agra.

The Acid Precipitations

In atmospheric chemistry the term precipitation refers to rain, snowfall, fog, mist and dry deposition of acid particles. The acid precipitation is of two types.

1. Wet Acid precipitation which includes rain, snowfall, fog, mist etc.
2. Dry Acid Precipitation which includes acid precursor gases like SO_2 , Nitrogen Oxides (NO_x), Nitrate and Sulphate.

The background or normal pH of unpolluted rain water is estimated to be 5.6 buffered by atmospheric carbon dioxide. Charles and Rodhe (1982) have shown that if there were no ammonia and $CaCO_3$ in the atmosphere, the pH of the rain water due to natural sulphur compounds alone would be around 5. In large dry land areas having plenty of basic substances the pH of rain water could be 6 percent. Human activity is responsible for a decrease in pH of rainwater. The oxides of nitrogen and sulphur due to their atmospheric oxidation products nitric and sulphuric acids respectively increase the acidity and hence decrease pH. The precipitations which are of pH lower than 5.6 are termed acid precipitations or simply called as acid rain. The pH of acid rain is generally between 5 and 4. In exceptional cases the pH could be as low as 1.7 which was recorded in Pitlochry, Scotland on April 10, 1974.

The Historical Perspective:

The term acid rain was first coined by R.A. Smith (1872) to describe the extent of pollution in the air of Manchester which damaged vegetation, bleached the colour of the fabrics and corroded metals. Our present knowledge of the chemistry of acid rain is based on the work of E. Gorham (1955) in Canada and England.

He established that the main cause of acid rain is sulphuric acid. In 1961, Svante Odén established a network of more than 150 monitoring stations to measure water surface chemistry. His results indicated that the most of Europe received acid rain, the surface water and precipitations were becoming more acidic and that

the long distance transport of oxides of sulphur and nitrogen (100 - 2000 KM) was taking place. This revelation led to a mounting universal concern (1968, 70). The UN Conference on Human Environment (1972) first alerted the world about the danger of acid rain problem.

The Acid Rain: An International Issue:

The acid rain has international dimensions as the countries which produce acid precursor gases are not the only sufferers, but the countries which have controlled the SO_2 and NO_x level at an acceptable level are also receiving acid precipitation.

In this regard the following observations are worth noting :

- (i) Generally the areas which emit SO_2/NO_x receive acid rain
- (ii) The areas which have no SO_2/NO_x emission sources also receive acid rain.
- (iii) In some areas the local emissions have decreased but acid rain has increased.

The last two observations can be explained only through long range transport of the acid precursor gases to areas not producing these. This is the only way to explain the pollution of arctic circle which has hardly any industry worth the name.

The Chemical Composition of Acid Rain:

The results of chemical analysis of acids present in the atmospheric acid precipitations are given in Table - 1. The percentage of acids present in acid rain in different countries.

Table - 1.

Country	% H_2SO_4	% HNO_3	% HCl
North Eastern US	62	32	6
Scandinavia	70	30	-
Scotland	71	29	-

The pollutants responsible for acid precipitation are listed below

- (i) Primary Pollutants - SO_2 , NO_2 hydrocarbons and suspended particulate matter (spM)
- (ii) Secondary Pollutant - H_2SO_4 , Ozone etc. The main sources of pollutants are as follows :

(i) Sources of SO_2

(a) **Natural Sources** - These include Volcanoes, oceans, biological decay of organic waste products and forest fires. The H_2S of natural origin is oxidised into SO_2 in atmosphere.

(b) **Anthropogenic Sources** - The major man-made sources responsible for emission of SO_2 are thermal power plants, processes involving combustion of fossil fuels like coal, primary metal extraction units and some chemical industries.

UNEP estimates that the all global anthropogenic sources emit about 75-100 million tonnes of SO_2 annually while natural sources contribute between 80-288 million tonnes per annum. It must be pointed that while the natural emissions remain widely distributed the man-made emissions are confined to a limited area only.

(ii) Sources of NO_x

(a) Natural Sources:

The most important natural sources of oxides of nitrogen are chemical decomposition of nitrates, biodegradation of proteins, volcanoes and lightning. The high volcanic and lightning temperatures make the atmospheric nitrogen and oxygen combine to give NO .

(b) Anthropogenic Sources -

The high temperature combustion of fossil fuels like oil, coal and natural gas and automobile exhaust emissions. It is estimated that while anthropogenic sources release about 75-90 million tonnes of NO_x per annum, the natural sources contribute between 1-20 million tonnes per annum.

II. DISCUSSION:

This study was carried out in two phases

- (i) Aqueous phase oxidation
- (ii) Gas phase oxidation

Aqueous phase oxidation

Different steps of formation of H_2SO_4 discussed with their rate constants and final derivation of s(VI) rate is :

$$d \text{S(VI)}/dt = (1 + K_{A1}/[\text{H}^+] + (K_{A1} + K_{A2})/[\text{H}^+]^2$$

Metal ion catalysed autooxidation

Fe(III) catalysis :

The reaction of S(VI) with O₂ is very slow in the absence of metal ion and light. Fe(III) because of its ability to coordinate with SO₂ and O₂ strongly catalyses the autooxidation.

The following two principle mechanism have been proposed for the Fe catalysed reaction.

(I) One electron free radical reaction

(II) Two electron polar reaction involving ternary complexes comprised of the transition metal, S(IV) and molecular oxygen.

The final rate expression is :-

$$-d [SO_3^{2-}]/dt = k [M^{n+}]^{\alpha} [SO_3^{2-}]^{\beta} [O_2]^{\gamma}$$

the reaction orders α , β and γ vary from 0.5 to 1.5 .

Mn(II) catalysis :

The Mn(II) catalysed autooxidation exhibits complex kinetic behaviour. The rate of disappearance of S(IV) is given by

$$-d [S(IV)]/dt = k [Mn^{2+}][SO_3^{2-}]$$

Cu(II) catalysis :

The Cu catalysed autooxidation has been studied by large number of workers and the rate law obtained by these are as follows -

$$-d [S(IV)]/dt = k [Cu^{2+}][SO_3^{2-}]$$

In each case the rate doesnot depend upon [O₂].

Co(II) and Co(III) catalysis :

The empirical rate law by different workers are summarised below-

By Chen and barron

$$-d [S(IV)]/dt = k [Co^{3+}]^{1/2} [SO_3^{2-}]^1 [O_2]^0$$

By sawicki and barron

$$-d [S(IV)]/dt = k [Co^{3+}]^{1/2} [SO_3^{2-}]^2 [O_2]^2$$

By bengtsson and bjerle

$$-d [S(IV)]/dt = k [Co^{3+}]^{1/2} [SO_3^{2-}]^{3/2} [O_2]^0$$

By yagi and inoue

$$-d [S(IV)]/dt = k [Co^{3+}]^{1/2} [SO_3^{2-}]^1 [O_2]^1$$

Gas phase oxidation;-

In the troposphere, sulfur dioxide absorbs light in the UV region from solar radiations the absorption of radiation from wavelength region 33300-4000 Å⁰ results in the formation of different photo chemical reactive species of SO₂. This reacts with active species of O₂ to yield

SO₃. On reacting with free OH produced from water molecule it gives the rate law-

$$-d [SO_2]/dt = k_3 [OH][SO_2] [M]$$

As the pressure increases the rate becomes less sensitive to the concentration of M. At constant pressure the above equation follows second order.

III. CONCLUSION

Atmospheric SO₂ plays an important role in acid rain. Metal ion present in atmosphere further increases intensity of acid strength in precipitation. In order to reduce acid rain effluents in water and air has to be reduced.

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