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– CHEMICAL EDUCATION

PHOTOCHEMICAL AIR POLLUTION AND ITS EFFECTS ON PLANT AND HUMAN LIFE

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ABSTRACT

Air pollution is the excessive concentration of foreign matter in the air, which adversely affects the well being of an individual or causes damage to property. Photochemical air pollution due to formation of photochemical smog is restricted to highly motorised areas in metropolitan cities like Los Angeles. It occurs under adverse meteorological conditions, when the air movement is restricted. Photochemical smog is a complex mixture of several compounds. Among its various constituents, ozone and PAN (peroxy acetyl nitrate) are significant. Even though ozone is the major oxidizins agent in smog, there are small amounts of other agents, which vary in quanitity and interfere with ozone determination. On account of this, all oxidizing compounds in smog with oxidizing power more then molecular oxygen are combined and known as oxidants. Smog is caused by the interaction of some hydrocarbons and oxidants under the influence of sunlight giving rise to dangerous peroxy acetyl nitrate (PAN). Its main constituents are nitrogen oxides, PAN, hydrocarbons, carbon monoxide and ozone. Photochemical air pollution causes reducing visibility, eye irritation, damage to vegetation, cracking of rubber, fading of dyes etc.

Key words: Oxidants, Fog, Smog, PAN, Hydrocarbon, Ozone, Photochemical reaction, Nitric oxide, Meteorology.

INTRODUCTION

Air pollution is basically the presence of foreign substance in air. Smog is a combination of two words- smoke and fog. Photochemical smog is restricted to highly motorised areas in metropolitian cities, e. g. Los Angels. It occurs under adverse meteorological conditions, when air movement is restricted[1].

Photochemical air pollution

Photochemical smog is formed due to photochemical oxidation of hydrocarbons and nitrogen oxides. Among the theories proposed to account for the formation of smog, theory given by Prof. A. J. Haagen Smit found was to be generally acceptable as it is very

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comprehensive[2]. It has been found that at the time of photochemical smog formation, there is a considerable increase in the amount of ozone and oxidant material. The ozone is not found in appreciable amounts at night, but only during the day. These facts clearly indicates that photochemical formation of ozone or oxidant from impurities, takes place due to the action of sunlight.

Nitrogen dioxide photochemical reactions

In the beginning, ultra-violet light energy is absorbed by NO_2 (Eq. 1). The highly energized molecule (NO_2*) then decomposes into nitric oxides and atomic oxygen (Eq. 2). The atomic oxygen reacts quickly with molecular oxygen to form ozone. However, unless some other energy-absorbent molecule is present, ozone will decompose rapidly. But if a third body (X) is present, a stable ozone molecule is formed (Eq. 3). If nitric oxide is present, it reacts with ozone to form NO_2 and oxygen molecule (Eq. 4).

$$NO_2 + hv \rightarrow NO_2^* \quad \ldots(1) \qquad NO_2^* \rightarrow NO + O \quad \ldots(2)$$

$$O + O_2 + X \rightarrow O_3 + X \quad \ldots(3) \qquad O_3 + NO \rightarrow NO_2 + O_2 \quad \ldots(4)$$

In the above reactions, NO_2 behaves like a catalyst[4].

Further, in the presence of certain hydrocarbons, other reactions take place. Some of the atomic oxygen, ozone and nitric oxide react with hydrocarbons to form a variety of products and intermediates with which even further reaction can probably take place. Some of the products formed are aldehydes like formaldehyde and acrolein, peroxides, and peroxy acetyl nitrate (PAN).

If nitric oxide is also present in the air, reaction takes place as follows –

$$NO + O_2 \rightarrow NO_2 + O_2 \quad \ldots(5)$$

If ozone is present in excess, then

$$2\ NO_2 + O_3 \rightarrow N_2O_5 + O_2 \quad \ldots(6)$$

If water vapour is present, then

$$N_2O_5 + H_2O \rightarrow 2\ HNO_3 \quad \ldots(7)$$

Thus nitric acid may be formed.

Sulpher dioxide photochemical reactions

Ozone may be formed in the atmosphere as a byproduct during the photochemical oxidation of sulphur dioxide to sulphuric acid. The reaction takes place as follows –

$$SO_2 + hv \rightarrow SO_2^* \quad \ldots(8) \qquad SO_2^* + O_2 \rightarrow SO_4 \quad \ldots(9)$$

$SO_4 + O_2 \rightarrow SO_3 + O_3$ …(10) $SO_3 + H_2O \rightarrow H_2SO_4$ …(11)

The quantum efficiency for this process is low.

Photochemical reactions of aldehydes

The photochemical oxidation of aldehydes can be represented as follows –

$$RCHO + hv \rightarrow RCHO^* \quad \ldots(12)$$

$$RCHO^* + O_2 \rightarrow RCO_3H \quad \ldots(13)$$

$$RCO_3H + O_2 \rightarrow RCOOH + O_3 \quad \ldots(14)$$

The primary photochemical decomposition of aldehydes produces organic free radicals. For example, acetaldehyde decomposes into methyl and formyl radicals.

$$CH_3CHO + hv \rightarrow {}^{\bullet}CH_3 + HCO^{\bullet} \quad \ldots(15)$$

Similarly, acetone decomposes into methyl and acetyl radicals.

$$(CH_3)_2CO + hv \rightarrow {}^{\bullet}CH_3 + CH_3CO^{\bullet} \quad \ldots(16)$$

Effect of photochemical smog

The effects of photochemical smog on human beings, plants and materials have been studied where it usually occurs. Additional information has also been obtained by stimulating photochemical smog in environmental chambers[3]. Following are the important effects of photochemical smog –

(i) Eye irritation: Probably, the compounds responsible for eye irritation are formaldehyde, acrolein, PAN and peroxy benzoyl nitrate.

(ii) Vegetation damage: The effects observed are silvering and bronzing of underside of leaves followed by collapse of cells, and necrosis. Growth retardation has also been reported. The three principal phytoxicants are ozone, nitrogen dioxide and PAN. This has resulted in economic loss.

(iii) Visibility reduction: This is perhaps the most commonly observed effect of photochemical smog. The aerosol particles causing the photochemical smog contain compounds of carbon, oxygen, hydrogen, nitrogen, sulphur, and halides.

(iv) Cracking of rubber: This is primarily due to the ozone constituents of photochemical smog. An important economic effect of smog is deterioration of the side walls of automobile tyres. To overcome this problem, an antiozonant is being used.

(v) Fading of dyes: This is another important economic effect of photochemical smog.

Photochemical smog is a complex mixture of several compounds. Among its various constituents, ozone and PAN (peroxy acetyl nitrate) are significant. Photochemical air pollution occurs predominantly in highly motorised areas and where inversion conditions prevail in the atmosphere. The size of the particles is about 0.3 μ. The liquid phase is largely made up of organic matter.

CONCLUSION

Photochemical air pollution is caused due to photochemical oxidation of hydrocarbons and nitrogen oxides. It has been found that at time of photochemical smog formation, there is a considerable increase in the amount of ozone and oxidant material. Facts clearly indicate that photochemical formation of ozone or oxidant from impurities, takes place due to the action of sunlight. The nature of the photochemical reactions that takes place in the atmosphere depends on a number of factors like light intensity, hydrocarbon reactivity, ratio of hydrocarbons to nitric oxide, presence of light absorbers, and metrological variables. Photochemical air pollution shows its effects like eye irritation, vegetation damage, visibility reduction, cracking of rubber and fading of dyes[4].

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