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PHOTOCHEMICAL SMOG

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ABSTRACT

Photochemical smog is a type of smog produced when ultraviolet light from the sun reacts with nitrogen oxides in the atmosphere. It is visible as a brown haze, and is most prominent during the morning and afternoon, especially in densely populated, warm cities. In this review, we shall be discussing it in detail, it's health hazards and abatement strategies.

KEYWORDS: Nitrous oxide, Nitrogen dioxide, nitrogen trioxide, dinitrogen pentoxide, alkyl nitrite, PAN

INTRODUCTION

To fully appreciate photochemical smog formation, one must recognize that nitrogen is transformed between many different substances in the atmosphere. Automobile exhausts release nitrous oxide (NO) along with small amounts of nitrogen dioxide (NO₂). These two substances form the starting materials for a vast array of chemical reactions that lead to products with higher oxidation states. In a straight forward process, nitrogen oxide (NO) is converted to nitrogen dioxide (NO_2), nitrogen dioxide is converted into nitrogen

trioxide (NO3) and nitrogen trioxide is converted into dinitrogen pentoxide (N_2O_5). Each of these four simple nitrogen oxides then reacts through a photochemical process, or direct physical contact, with atmospheric substances to form an impressive list of biological irritants. The list of irritants include: 1. alkyl nitrite 2. peroxyalkyl nitrate 3. alkyl nitrate 4. peroxyacetyl nitrate 5. nitrous acid 6. peroxynitric acid 7. nitric acid and 8. ammonium nitrate. These chemical transformations are shown graphically in figure 1.





The substances that react with nitrogen oxides to form oxidants (the final product of photochemical smog) are trace hydrocarbons (from incomplete combustion) and the hydroxyl radical. The necessary ingredients for photochemical smog formation are 1. Nitrogen oxides 2. sunlight and 3. hydocarbons. Photochemical smog formation proceedes through a sequence of reactions, all involving a free radical mechanism. Free radicals are generated by photodisassociation of nitrogen dioxide, a process that generates ozone and oxygen atoms. Oxygen atoms react with water to form hydroxyl radicals, which in turn react with hydrocarbons to form hydrocarbon radicals. Oxidation of hydocarbons by the hydroxyl radical leads to the formation of aldehydes. The aldehvdes are oxidised further to form aldehvde peroxides and aldehyde peroxyacids. These final subastances are the compounds that are so irritating to sensitive biological tissues and cause most of the health problems associates with photochemical smog.

General reaction of photochemical smog

eq. $1 NO_2 + hv \rightarrow NO + O$ eq. $2 O + O_2 + M \rightarrow O_3 + M$ eq. $3 NO + O_3 \rightarrow NO_2 + O_2$

This is a cyclic process that needs light and nitrogen oxides to generate oxygen atoms. Once formed, the oxygen atoms react with water to form hydroxyl radicals. The hydroxyl radicals then react with hydrocarbons according to equation 5 through it to form peroxyacyl nitrates (or PAN).

eq. 4 O*+ $H_2O \rightarrow 2 OH^*$ eq. 5 RH+ OH* $\rightarrow H_2O + R^*$ R*+ $O_2 \rightarrow RO_2^*$ very fast eq. 6 $RO_2^* + NO \rightarrow NO_2 + RO^*$ RO*+ $O_2 \rightarrow R'CHO + HO_2^*$ very fast

eq. 7 R'CHO + OH* \rightarrow R'CO* + H₂O R'CO* + O₂ \rightarrow R'C(O)O₂* very fast eq. 8 R'C(O)O₂* + NO₂ \rightarrow R'C(O)₂NO₂

In summary, this is what happenens in photochemical smog formation

- 1. Nitrogen oxides generate oxygen atoms
- 2. Oxygen atoms form hydroxyl radicals
- 3. Hydroxyl radicals generate hydrocarbon radicals
- 4. Hydrocarbon radicals form hydrocarbon peroxides
- 5. Hydrocarbon peroxides form aldehydes
- 6. Aldehydes form aldehyde peroxide
- 7. Aldehyde peroxides form peroxyacynitrites

Health Hazards of Photochemical Smog

Photochemical smog is capable of inflicting irreversible damage on the lungs and heart. Even short-term exposure to photochemical smog tends to have ill effects on both the young and the elderly. It causes painful irritation of the respiratory system, reduced lung function and difficulty breathing and wheezing. Photochemical smog can irritate and inflame pulmonary membranes, causing chest pains, coughing and throat irritation. High levels of smog also trigger asthma attacks because the smog causes increased sensitivity to allergens, which are triggers for asthma. It can lead to lethal disease like lung cancer.

Abatement Strategies of Photochemial Smog

Since photochemical smog is caused by various oxides of nitrogen being emitted by automobiles and fossil fuels, it can be reduced by walking or taking public transportation. Switching off electronics and air conditioning when not in use. Prevent high usage of coals, which results in heavy smog. We can also apply **Green Chemistry** to reduce photochemical smog by using alternate fuels like CNG which causes less pollution and by planting certain plants like *Pinus*, *Vitis*, *Pyrus* because these plants metabolise nitrogen oxide (NO).

CONCLUSION

Much is being done to control, monitor and rectify the damage done by pollutants. The problems are diverse and some are only being recognised but it is important to keep a close control over pollutants so that we can maintain the enviornment in an acceptatble condition for future generations.

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