4.2 Formation Mechanism of Air Pollutants

4.2.1 Introduction

It is well known that, among air pollutants, there are primary pollutants which are released directly by the human activities, and secondary pollutants which are formed by the reaction of primary pollutants in the atmosphere. In this chapter, the mechanism of formation and transformation of the secondary pollutants will be described, particularly the formation of photochemical ozone, the atmospheric chemical reaction involving hydrocarbons, and the reaction involved in the acid rain.

4.2.2 Photochemical Reaction of Ozone Formation

The reactions involved in the formation and transformation of secondary pollutants are mainly the formation reaction of photochemical smog in which solar energy is added to the primary pollutants, i.e. the oxides of nitrogen (NOx) and the hydrocarbons (HC). NOx, which is composed of NO (nitrogen monoxide) and NO_2 (nitrogen dioxide), has rather broad range of concentration, because its source is rather maldistributed and it has only a short life in the atmosphere. Generally, its concentration is 20-500 ppb (ppb is a thousandth of ppm) in the urban area, 1-10ppb in the rural area, and 0.05-0.2 ppb for the background including on the sea. The reactivity of NOx is very high in the atmosphere, so its life is very short. It involves in almost all reactions in the atmosphere both directly and indirectly to have an important role. Particularly, NOx has a major role in the formation of ozone in the troposphere, as revealed in the occurrence of photochemical smog in the urban area. The presence of NOx is very important, because only NO_2 can be the potential source of ozone in the troposphere.

If there is a fractional amount of NOx in the air of troposphere, it receives solar radiation and the ozone is formed via the formation of NO, as indicated by Eq. (7) and (8):

$$NO_2 + h\nu \rightarrow O(^3P) + NO \quad \cdots\cdots (7)$$

$$O(^3P) + O_2 \rightarrow O_3 \quad \cdots\cdots (8)$$

where O (^{3}P) represents the oxygen atom in the ground state. However, if those are the only reactions, the ozone concentration would attain a steady state and does not reach to any extremely high value, because the reaction (9) will occur in which ozone will be destroyed by NO produced in the reaction (7):

$$O_3 + NO \rightarrow NO_2 + O_2 \quad \cdots\cdots (9)$$

However, if there are any hydrocarbons in the atmosphere, NO will be transformed to NO_2 by peroxyl radicals such as $HO_2\cdot$ and $RO_2\cdot$, produced by the reactions of hydrocarbons, without destroying ozone, and the reaction indicated in Eq. (10) will proceed.

$$NO + HO_2\cdot \text{ or } RO_2\cdot \rightarrow NO_2 + \cdot OH \text{ or } RO\cdot \qquad (10)$$

NO_2 produced in this reaction is then used to form ozone through reactions of Eq. (7) and (8). In Eq. (10), R is a group derived from hydrocarbons such as alkyls. As a result, the concentration of ozone becomes high under the condition of strong solar radiation.

Chemical reactions in the troposphere are frequently initiated by $\cdot OH$ radicals. Particularly, alkanes and aromatic hydrocarbons, which do not react with ozone, are destroyed by the reaction with $\cdot OH$ radicals. OH radicals in the troposphere are primarily produced through the reactions represented by Eq. (11) and (12), and are reproduced by radical chain reactions involving NO_x and hydrocarbons, as shown in Eq. (7), to join in the reaction again:

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \qquad (11)$$

$$O(^1D) + H_2O \rightarrow 2\cdot OH \qquad (12)$$

In the above equations, $O(^1D)$ is the oxygen atom in the excited state. The oxygen atom in the ground state, $O(^3P)$ would not react with water.

4.2.3 Reaction of Hydrocarbons

The reaction shown in Fig.4.2.1 is a typical photo-oxidation reaction of a common hydrocarbon, alkane. Through such a chain reaction, the carbon in hydrocarbons is gradually oxidized to carbon dioxide, and the ozone is accumulated through $NO \rightarrow NO_2$ conversion, as described previously. For Type (b) products (peroxyl radicals), not only the oxidation of NO indicated in Fig.4.2.1 but also the formation of nitrate ester ($RONO_2$) through addition and rearrangement reactions of NO, as shown in Eq. (13), becomes important, when the chain of alkyl becomes longer or larger:

$$RO_2\cdot + NO \rightarrow [ROONO] \rightarrow [RONO_2]^* \rightarrow RONO_2 \qquad (13)$$

Also, Type (c) products, alkoxyl radical ($RO\cdot$) react mainly with oxygen, but they also produce nitrate esters and nitrite esters through NOx addition reaction, as shown in Eq. (14), when enough concentration of NOx exists:

$$RO\cdot + NO_2 \text{ or } NO \rightarrow RONO_2 \text{ or } RONO \qquad (14)$$

The nitrite ester is easily decomposed by visible light, and could start the chain reaction shown in Fig.4.2.1 by producing alkoxyl radicals. Thus, the nitrite ester is known to act as an important initiator for the photochemical reaction, if it is accumulated during the night by the reaction of Eq. (14) in conjunction with the ozone-olefin reaction or the reaction between NO_3 radicals and hydrocarbons [1].

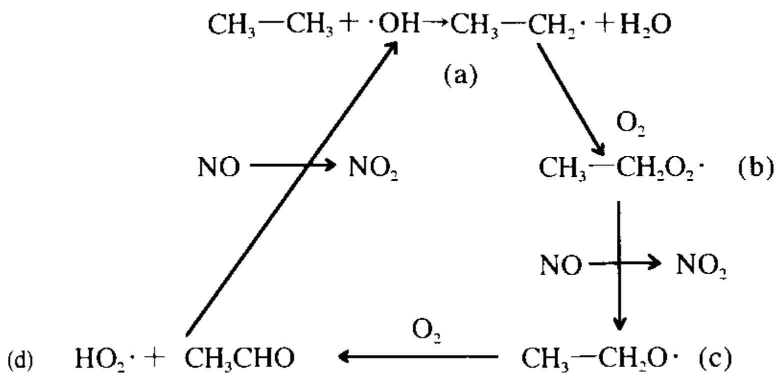

Fig.4.2.1 Photo-oxidation chain of hydrocarbon initiated by OH radical

Another important product that contains NOx is the compound called PAN. PAN was originally the generic name of peroxyacyl nitrate ($RC(=O)OONO_2$), but now frequently indicates peroxyacetyl nitrate ($CH_3C(=O)OONO_2$), the most important one among them. Its most important formation process is the one that starts with the reaction between acetaldehyde produced by photochemical reaction of hydrocarbons of molecular weight larger than ethane (or released as primary pollutants) and ·OH, as shown in Eq. (15) to (17).

$$CH_3CHO + \cdot OH \rightarrow CH_3CO + H_2O \quad \cdots\cdots \quad (15)$$

$$CH_3CO + O_2 \rightarrow CH_3C(=O)OO \quad \cdots\cdots \quad (16)$$

$$CH_3C(=O)OO + NO_2 \rightarrow CH_3C(=O)OONO_2 \quad \cdots\cdots \quad (17)$$

PAN is one of the photochemical oxidant, and a substance with a strong toxicity which gives visible damage to the plant and is also known to give damage to humans. Recently, its importance as a role for a nitrogen reservoir is pointed out [2]. Since the life of NOx in the atmosphere is very short, NOx would disappear through reactions in the vicinity of its source without traveling long distances (long range transport). However, once PAN is formed and moves to the upper layer where the temperature is low, its life becomes very long. For instance, the life of PAN is only 1.7 hours at the temperature of 20℃ (Its process of disappearance is mainly the thermal decomposition expressed by the reverse reaction of Eq.(17).), but it increases to 50 hours at 0℃ and 105 days at -20℃ [3]. Accordingly, it is quite probable that nitrogen would be transferred for a long distance in the form of PAN and then NO_2 would be released by its decomposition to involve into the photochemical reaction. Actually, a high concentration of ozone, often seen in early spring in the troposphere of a middle latitude region in northern hemisphere, is postulated to be caused by an ozone source produced by NO_2, which is produced as PAN has been accumulated and transferred during the winter and decomposed as temperature rises [4].

4.2.4 Atmospheric Chemical Reaction Associated With Acidification of Tropospheric Air (Acid Rain)

The acid rain is one of the environmental problems of global scale that is attracting a major concern. Although the acidification of rain itself is a problem, the fundamental problem is the acidification of tropospheric air, and the acid rain should be considered as only the outcome of the latter. Of course, the acidification of tropospheric air is caused by the increase of sulfur oxides and nitrogen oxides released from various human activities. Those compounds are oxidized in the atmosphere to form sulfuric acid and nitric acid, and those would be dissolved into rain water to form the acid rain.

The increase of NOx causes the increase of concentration of ozone or various oxidizing radicals ($\cdot OH$, $HO_2\cdot$, $RO_2\cdot$, etc.), and thus enhances the oxidizing capability of atmosphere. Together with the increase of precursor for acid substances, those materials are also causing the increase of acid substances in the atmosphere.

In the formation of acid substances, there are the formations of sulfuric acid through oxidation of SO_2 and of nitric acid through oxidation of NOx. In the oxidation of SO_2, the gas phase homogeneous reaction by OH radical, as shown in Eq. (18) to (20), as well as the reaction of SO_2 in solution after dissolved into water in cloud, fog or raindrops are both important. Hydrogen peroxide is performing a major role in the reaction in solution [5].

$$SO_2 + OH \rightarrow HOSO_2 \quad \cdots\cdots \quad (18)$$

$$HOSO_2 + O_2 \rightarrow SO_3 + HO_2 \quad \cdots\cdots \quad (19)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad \cdots\cdots \quad (20)$$

On the other hand, the formation process of nitric acid through oxidation of NOx is relatively simple, and the liquid phase oxidation reaction, seen in the case of SO_2, hardly occurs because NOx is not readily soluble in water.[6] The oxidation is considered to proceed primarily by three reactions as follows:

(1) Reaction with $\cdot OH$ radical

The role of $\cdot OH$ is important also in the formation of nitric acid, as shown in Eq. (21):

$$NO_2 + \cdot OH \rightarrow HNO_3 \quad \cdots\cdots \quad (21)$$

(2) Reaction of NO_3 radical

NO_3 radical is a highly reactive radical produced by the reaction between ozone and NO_2. Particularly, it has a very important role in the reaction of various organic compounds including hydrocarbons during the night time when the light is not available. NO_3 radical is converted to nitric acid by reacting with organic compounds such as hydrocarbons and aldehydes, as shown in Eq. (22):

$$NO_3 + RH \rightarrow HNO_3 + R\cdot \quad \cdots\cdots \quad (22)$$

(3) Reaction of N_2O_5

N_2O_5 is formed by the reaction between NO_3 and NO_2, and is acting an important role as one of the nitrogen containing pollutants in the reactions in the nighttime. N_2O_5 is, in a sense, a nitric acid anhydride, and capable of hydrolysis as shown in Eq. (23). Here, however, the rate constant of direct reaction with water vapor in the gas phase homogeneous system is less than 2×10^{-21} $cm^3\cdot molecule^{-1}\cdot s^{-1}$ [7], and is not important. However, the extinction process of NOx or the formation process of nitric acid would be accelerated with the existence of a surface, and it is important as a formation process of nitric acid in the open air.

$$N_2O_5 + H_2O \rightarrow 2\,HNO_3 \qquad (23)$$