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Influence of Nitrosyl-Sulfuric Acid on the Air Pollution Smog Formation

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요 약

연무의 생성과정을 다음과 같은 전제 아래 연구하였다. 즉 대기 중에서 이산화황과 이산화질소가 반응할 때, 수분 또는 안개가 존재하면 초기단계에서는 태양광선에 의하여 니트로실황산이 생성되며 이것이 분해하여 황산을 만든다. 즉,

$$SO_2^* + H_2O \longrightarrow H_2SO_3$$
$$H_2SO_3 + NO_2^* \longrightarrow HOSO_2ONO$$
$$HOSO_2ONO \longrightarrow H_2SO_4 + HNO_3$$

이때 생긴 질산은 유기과산화물과 반응하여 과산화니트로화합물을 만든다. 결과적으로 황산화물, 질소산화물, 유기산화물, 니트로화합물 및 산화제의 혼합물은 대기중에서 서로 작용하여 스목현상을 일으킨다. 이상과 같은 가정하에서 실험한 바 예기하였던 결과를 얻었다. 그리고 서울시내의 대기오염도를 측정하였던 바 황산화물의 오염도가 질소산화물보다 심하다는 사실을 알았다.

Abstract

The formation of smog was studied on the basis of the following hypothesis: when sulfur dioxide and nitrogen dioxide react each other in the atmosphere, nitrosyl-sulfuric acid will be formed at the initial stage by solar radiation in the presence of moisture or fog and then sulfuric acid will be formed by the decomposition of nitrosyl-sulfuric acid. That is,

$$SO_2^* + H_2O \longrightarrow H_2SO_3$$

$$H_2SO_3 + NO_2^* \longrightarrow HOSO_2ONO$$
$$HOSO_2ONO \longrightarrow H_2SO_4 + HNO_3$$

The nitric acid generated by the above reaction will react with organic peroxide and forms nitro peroxide compounds. Finally, the mixture of sulfur oxide, nitrogen oxide, organic peroxide nitro-compounds and oxidant will cause the formation of smog. A series of experiments have been performed and the results supported the above hypothesis as expected. In addition, a separate study has been carried out with regards to the air pollution in Seoul to confirm that sulfur oxide was more serious than nitrogen oxide.

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1. Introduction

Major air pollutants emitted into the atmosphere are nitrogen oxides(NO_X) and sulfur oxides (SO_X). Atmospheric pollution occurs mostly by the interaction of nitrogen dioxide, oxidant and sulfur oxides in the air. Sulfur compounds of major interest in air pollution are sulfur dioxide, sulfur trioxide, sulfurous acid, hydrogen sulfide, sulfuric acid and sulfate salts. The sulfur oxides are produced mainly by the combustion of fuels, particularly in fossil-fueled power plants, and are also emitted from motor vehicles.

Several studies on the interaction between sulfur oxides and other pollutants were made and it was reported that the smog formation or aerosol phenomenon in the atmosphere would occur by the interaction among sulfur oxides, water vapor and coagulated solid particles under solar irradiation. That is, sulfur dioxide in air would undergo a slow reaction under sunlight to form sulfur trioxide or sulfuric acid which would eventually contribute to the haze as well as the reduced visibility.

Various reaction mechanisms described by several authors for the generation of sulfuric acid by the oxidation of sulfur dioxide in air are mostly that these reactions will occur by sunlight and atomic oxygen or ozone. Gerhard and Johnston[1)] confirmed that sulfuric acid is formed through the interaction between sulfur dioxide and oxygen and steam under sunlight. He also reported that existence of nitrogen oxides in the reaction system did not show any effect on forming sulfuric acid.

The present author proposed that conversion of sulfur dioxide to sulfuric acid would take place through the formation of intermediate nitrosyl-sulfuric acid and the final product, sulfuric acid, would be formed by the decomposition of this intermediate. A series of experiments showed that the result confirmed the proposed mechanism.

Additionally, other experiments were carried out with regard to the air pollution in the metropolitan area of Seoul, Korea and it was noticed that the degree of contamination by sulfur oxides was more intense than by nitrogen oxides or other oxidants.

2. Nitrosyl-sulfuric acid and sulfuric acid formation

The reaction involved with SO_2 in the atmosphere could be anticipated in several ways. Though ozone (O_3) or excited oxygen (O_2^*) may be formed in the atmosphere under solar irradiation, it is very difficult for SO_2 to combine with ozone or excited oxygen under the presence or absence of moisture due to strong electronic bond in SO_2[3)]. The dissociation energy of SO_2 into $SO+O$ is 135kcal/mol(2100Å) and SO_2 will absorb 1950Å line easily to form excited sulfur dioxide (SO_2^*).

Through the decomposition of sulfur dioxide by ultra violet light Hill[5] oserved the formation of elemental sulfur and concluded that 94% of the decomposition was due to the 3130Å line. Photochemical studies of SO_2+O_2 mixture was also reported by Blacet[6] who obtained a quantum yield of about 1×10^{-3} from the decomposition of SO_2 by the 3130Å line. A probable reaction mechanism has been proposed by Blacet.

Johnstone[7] asserted that SO_2 changed into activated SO_2^* under solar irradiation and finally sulfur trioxide was formed through the interaction between oxygen and SO_4 which was generated from the interaction between SO_2^* and O_2. That is,

$$SO_2 + h\nu \longrightarrow SO_2^* \qquad (1)$$

$$SO_2^* + O_2 \longrightarrow SO_4 \qquad (2)$$

$$SO_4 + O_2 \longrightarrow SO_3+O_3 \qquad (3)$$

He ascertained that based on the data of 10~20 ppm SO_2 the percent conversion of SO_2 per hour was essentially constant and averaged 0.68% under artificial sunlight and that 0.1~0.2% of SO_2 was changed into SO_3 under natural intense solar irradiation in his experimental runs. He also confirmed that the presence of approximately 10% of NO_2 would not effect the additional conversion of SO_2 into SO_3. However, he explained that smog phenomenon was caused by SO_3 formation under the presence of water particles or fog when SO_2 was irradiated by sunlight.

Until now, a satisfactory research result has not been obtained with respect to smog phenomenon caused by reaction among SO_X, NO_X, oxidant, hydrocarbons and water particles in the outdoor atmosphere. It is merely recognized that metallic oxides such as Al_2O_3, CaO, Fe_2O_3, and V_2O_5 would promote the catalytic action of SO_2 with oxygen. Uronetal[8] verified catalytic oxidation of SO_2 by metallic oxides and eventual formation of sulfuric acid in the presence of moisture in the atmosphere. However, it is difficult to consider the presence of sufficient quantity of metallic oxides in the atmosphere to oxidize the SO_2. Particularly, it cannot be expected that there exists a powerful oxidation catalyst, such as V_2O_5, in the atmosphere.

It can be easily understood that sulfur oxides or sulfuric acid will react with reactive ammonia when it exists in the atmosphere to produce ammonium sulfate salt.

$$H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4$$

When the isolated atomic oxygen exists in the atmosphere, it will react with SO_2 or SO_2^* easily but it requires the presence of a third compound.

$$SO_2 + O + M \longrightarrow SO_3 + M$$

Atomic oxygen will be formed preferentially when a photochemical reaction occurs on the surface of the earth caused by nitrogen oxides[9]. In this case the formation of SO_3 is facilitated. The present author predicts that nitrosyl-sulfuric acid will be formed from the mixture of sulfur oxides and nitrogen oxides at the initial stage under solar irradiation in the presence of moisture and fog.

In general SO_2 would react with water particles either in the gas phase or in the liquid phase. When nitrogen oxides are present, the postulated mechanism includes the following set of reactions.

$$SO_2 + H_2O \longrightarrow H_2SO_3 \qquad (4)$$

$$H_2SO_3 + NO_2 \longrightarrow H_2SO_4NO \qquad (5)$$

The end product of reaction (5) is a violet acid. However, violet acid will be immediately changed into nitrosyl-sulfuric acid $HOSO_2\cdot ONO$ due to its instability[10]

$$2H_2SO_4NO + 1/2O_2 + NO_2 \longrightarrow 2HOSO_2\cdot ONO + H_2O(NO) \qquad (6)$$

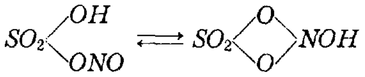
Once a nitrosyl-sulfuric acid is formed, sulfuric acid would be produced continuously by the following reaction.

$$2HOSO_2\cdot ONO + SO_2 + 2H_2O \longrightarrow 2H_2SO_4NO + H_2SO_4 \qquad (7)$$

Continuous production of H_2SO_4 will be expected by recycling violet acid that is formed by the reaction (7).

Particularly, the solubility of SO_2 gas in the liquid phase reaction mixture will be increased with a decrease in the sulfuric acid concentration and that of nitrogen oxides will be reversed. However, it is difficult to expect such a liquid phase reaction in general in the atmosphere.

Nitrosyl-sulfuric acid consists of NO^+ and $H_2SO_4^+$ and a mixture of structural isomers, $HOSO_2\cdot ONO$ and $OHSO_2\cdot NO_2$, which are in equilibrium as follows:



$$SO_2\langle^{OH}_{ONO} \rightleftarrows SO_2\langle^{O}_{O}\rangle NOH$$

The nitrosyl-sulfuric acid is stable in dry air but decomposes by moisture or water particles. [cf. reaction(7)] Probability of reactive collision between SO_2 and NO_2 in the gas phase reaction under the presence of moisture is not significant.

In general, formation of nitrosyl sulfuric acid isexpected under the following conditions:

1. Liquid N_2O_4 reacts with concentrated sulfuric acid at room temperature.
2. N_2O_4 gas reacts with concentrated sulfuric acid.
3. SO_2 reacts with concentrated nitric acid at room temperature.
4. Concentrated nitric acid reacts with concentrated sulfuric acid.
5. NOCl reacts with concentrated sulfuric acid.

These reactions cannot be expected to occur in an ordinary atmosphere. However, once combustion flue gas is emitted into the atmosphere, NO would be changed into NO_2 immediatly[11].

$$2NO + O_2 \longrightarrow 2NO_2 \qquad (8)$$

The association of NO_2 would be accelerated at low temperature and high pressure. For example, 50% of NO_2 associates at −10°C and 4 atm.

$$2NO_2 \longrightarrow N_2O_4 + 12.8\text{kcal}$$

Therefore, this reaction will not be expected to take place in the atmosphere. NO was reported to change into N_2O_5 in the atmosphere[12] by the following reactions:

$$NO_2 + NO \longrightarrow N_2O_3$$
$$N_2O_3 + O_2 \longrightarrow N_2O_5$$

and N_2O_5 converted into N_2O_4 through the reaction with the atomic oxygen[13].

$$N_2O_5 + O \longrightarrow N_2O_4 + 1/2O_2$$

McHaney insisted that NO_2 would react with H_2O to produce nitric acid in the gas phase under the presence of water particles when NO_2 is present in the atmosphere,

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO \qquad (9)$$

and equilibrium constant for the reaction was reported[14] as

$$(K)_{300°K} = \frac{[HNO_3]^2[NO]}{[NO_2]^3[H_2O]} = 0.004\text{atm} \quad (10)$$

He also found out that 0.5% of NO_2 had been converted to HNO_3 under high concentration of water particles in the reaction system and at room temperature.

On the other hand, nitric acid will be formed by the following reaction.

$$NO_2' + -OH \longrightarrow HNO_3 \qquad (11)$$

NO_2' is formed by solar irradiation in the atmosphere when NO_2 becomes activated[15], and −OH is formed by the following reactions[16].

$$H_2S + O \longrightarrow -OH + HS \qquad (12)$$
$$O + H_2O \longrightarrow 2(-OH) \qquad (13)$$

The reaction mechanism concerning the formation of HNO_3 and its decomposition in the atmosphere have been also studied by Sohn[17].

The following reaction will be expected to take place easily by O, O*, NO* and N_2O_4 produced by each of the above reactions.

$$H_2SO_3 + NO_2^* \longrightarrow H_2SO_4\cdot NO \qquad (14)$$

$$N_2O_4 + H_2SO_4 \longrightarrow HO\cdot SO_2\cdot ONO + HNO_3 \qquad (15)$$

Formation of the nitrosyl-sulfuric acid by photochemical reaction in the atmosphere will be expected mainly from reaction (14). On the other hand, nitrosyl-sulfuric acid hydrolyzes to sulfuric and nitric acids in water solution.

$$HO\cdot SO_2\cdot ONO_2 + H_2O \longrightarrow H_2SO_4 + HNO_3 \qquad (16)$$

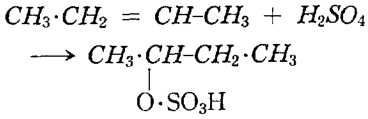
Therefore, sulfuric acid will be formed by nitrosyl-sulfuric acid decomposition reactions (7) and (16), and those reactions occur in the atmosphere where there exist moisture and water fog.

The formation of sulfuric acid in the atmosphere as stated above is very important in foggy weather, and those reactions occur in the upper zone of fog by photolysis; the photolysis products would cause the production of nitrosyl-sulfuric acid after diffusing to the surface of the earth. In general, when we observe the smog phenomenon, it can be recognized that the smog particles diffuse to the surface of the earth from the upper zone of fog and thus the visibility is gradually reduced. The smog phenomenon does not become severe under overcast conditions because the sunlight will be intercepted by clouds and consequently the photochemical reaction caused by oxidation of SO_2 will not take place even if the relative humidity is very high in the atmosphere.

3. Aerosol smog formation

When alkyl radicals or unsaturated hydrocarbons exist in the atmosphere, they may produce the nitric esters and peroxy nitric esters with NO_2. Subsequent reaction of these ester with SO_3 or H_2SO_4 would produce sulfonic compounds or sulfates.

$$CH_3\cdot CH_2\cdot COOO- + SO_3 \longrightarrow CH_3\cdot CH_2\cdot COOOSO_3H \qquad (17)$$



$$CH_3\cdot CH_2 = CH\text{-}CH_3 + H_2SO_4 \longrightarrow CH_3\cdot \underset{\underset{O\cdot SO_3H}{|}}{CH}\text{-}CH_2\cdot CH_3 \qquad (18)$$

These products, especially sulfonic compounds, would act as surface active agents for hydrocarbon, water particle and peroxides. Promotion of dissolution and emulsification by these agents would facilitate the diffusion of dusts within the mixture. This is equivalent to the formation of aerosol-type smog.

Coagulated aerosol smog particles are formed by the above reactions and the state of resulting emulsion caused by surface activity of sulfonic acid will not be destroyed and these particles will float in the atmosphere as long as contact with the earth surface or any other obstacles is maintained. In this case, however, the action of sulfonic acid will be effective after an intense solar irradiation is applied to the hydrocarbons; in other words, after much photochemical reactions have resulted. Theoretically therefore, the aerosol smog phenomenon cannot be expected at dawn or midnight. It would be expected during the day time only.

4. Experimental apparatus

The reaction chamber was made of glass and lined with polyethylene film inside, having a volume of 20 liters with a plexiglass window. The gas inlet and outlet tubes were made of polyvinyl chloride (PVC).

It was assumed that the plexiglass transmitted most of the ultra violet above 2950Å and the absorption of SO_2 gas by PVC pipes were negligible. In order to take the gas sample from the chamber a sampling pipe was attached to the side of the chamber.

The aerosol sample was drawn out by a vacuum pump. In order to chill the steam in the reaction chamber a cooling pipe was installed at the bottom of the chamber, and both the temperature and humidity were measured whenever desired.

5. Experimental procedure

At the beginning of each test, filtered air was passed through the reaction chamber for 10 minutes. In this case, the filtered air was prepared by passing air through the activated charcoal bed in order to remove acid and alkali substances, and then passed again through the cellulose-asbestos type filter paper to absorb the aerosol.

Provision was made for preliminary photochemical reaction by adding the desirable amount of NO_2 gas into the chamber and then applying the sunlight irradiation on the air-gas mixture with the inlet and outlet pipe closed.

Steam was finally injected into the chamber to obtain the saturation humidity. The steam caused the expansion of the balloon that was attached to the top of the chamber. The balloon shrunk when the moisture was condensed in the chamber.

If the fog disappeared during the reaction, steam was added again into the chamber and the condition was controlled to form a fog by cooling, and then photochemical reaction proceeded continuously. The amount of NO_2 gas was adjusted in terms of the quantity of NO_2 gas for producing nitrosyl-sulfuric acid in this experiment, because it seldom contained over 1 ppm of NO_2 gas in the actual atmosphere. In other words, a theoretical equivalent quantity of NO_2 gas for 1 ppm of SO_2 gas is 0.72 ppm when a chain reaction is not considered.

The reaction time was adjusted every 30 minutes. After the reaction proceeded, the reacted gas was drawn out from the chamber and passed through water to collect the sulfuric acid, and to sum up the sulfuric acid drops which were deposited on the walls of the vessel by rising with water, and then the total acid content was analysed. The quantity of the sulfuric acid was determined by acid metric procedure using a methyl red-methylene blue as an indicator.

The aerosol was drawn into water in order to detect the nitrosyl-sulfuric acid, and analysis was made to detect the HNO_3 and H_2SO_4 produced by decomposition of nitrosyl-sulfuric acid with water. The composition of the nitrosyl-sulfuric acid was determined by comparing the ratio of HNO_2 and H_2SO_4 contents.

In this experiment various runs were made by changing SO_2 content under the presence of NO_2 and water fog, and the result of interaction with respect to time changes were investigated.

6. Results and Discussions

Data obtained from the reaction of sulfur dioxide-air mixtures containing 1, 5, 10, 20 ppm under the presence of 1 ppm NO_2 and fog are shown in *Fig.* 1. Duplicate runs showed a maximum deviation of 20–30% from the average due to the difficulty in controlling the humidity and forming a foggy condition. The results showed a slow reaction rate during the first one hour which can be considered as the induction period.

There is an approximately linear increase in sulfuric acid aerosol formation with time for a given SO_2 concentration after the induction period, although the reaction rate slowed down again after 4 hours of reaction time. This indicates that there exist limitations for the formation of H_2SO_4 through photochemical reaction. The percent conversion per hour is essentially constant and averages 53% during the period of photochemical reaction.

A typical natural water fog contains about 300 mg of water per cubic meter with an average particle size of 20 microns, or only about 70 particles per cubic centimeter.

1 ppm SO_2 concentration can be denoted as;

1 ppm $=2860\mu g/m^3$ (0°C, 760mmHg)

Therefore, the chances for the reactive collision among SO_2, NO_2 and water particles are expected to be high if SO_2 gas were completely diffused in the atmosphere in water fog. However, the aerosol mass concentration was calculated to be 20-30mg/m^3 in this experiment. Under these conditions both the photochemical acid fog and the natural water fog would have approximately the same liquid surface area per cubic centimeter of air. Thus, if the total amount of SO_2 absorbed controls the rate of reaction in the liquid phase, a larger rate of reaction would be expected for a natural water fog than was found in the artificial photochemical fog.

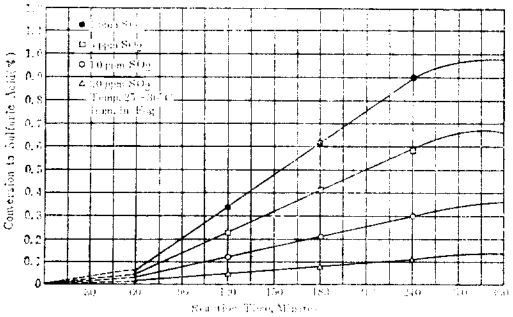


Fig. 1 The conversion of sulfur dioxide to sulfuric acid in solar irradiation

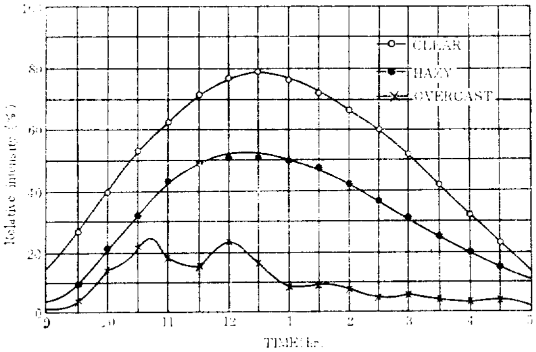


Fig. 2. Ultraviolet intensity in sunlight

In the case of natural fog, the photochemical reaction would receive the influence of interception of the ultra violet line by fog. The variation of ultraviolet intensity from 9 A.M. to 5 P.M. for typical clear, hazy or overcast day in summer was shown in *Fig.* 2. *Fig.* 2. shows that the ultra violet intensity of a foggy day is about 60% of that of the clear days, and is about 30% in an overcast day. Thus, the smog phenomenon would be expected on a foggy day, but it cannot be expected on an overcast day.

A series of runs were carried out to investigate the influence of NO_2 quantity to the photochemical reaction in which 1, 2, and 4 ppm of NO_2 were added along with 1, 5, and 10ppm SO_2, respectively. The results of the photochemical reaction data are shown in *Fig.* 3. *Fig.* 3 shows that, although the process of sulfuric acid formation is similar to that shown in *Fig.* 1, the sulfuric acid formation rate is increased as much as the concentration of NO_2 gas. However, the rate of increase is about 50% compared with each line shown in *Fig.* 1. If there are relatively large amounts of SO_2 and NO_2 existing in the atmosphere, the air pollution would be expected to be serious.

Fig. 4 shows the results of sulfur oxides(SO_X) concentrations measured in Seoul, Korea, from 1975 to 1976. The result of observing the air pollution phenomenon in Seoul varies with season, and the SO_X concentration is higher in winter than in summer, and the SO_X contamination is more serious in the downtown areas than in suburban areas.

These research results cannot represent the entire condition of the Seoul area because the data were obtained in the Hannamdong district, but it shows that the SO_X concentration approaches the public nuisance level. However, the

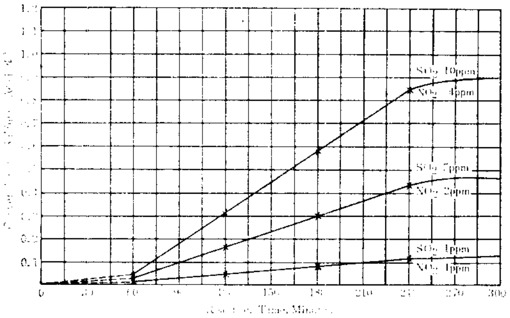


Fig. 3. **The conversion of sulfur dioxide to sulfuric acid in solar irradiation in the presence of NO_2 gas**

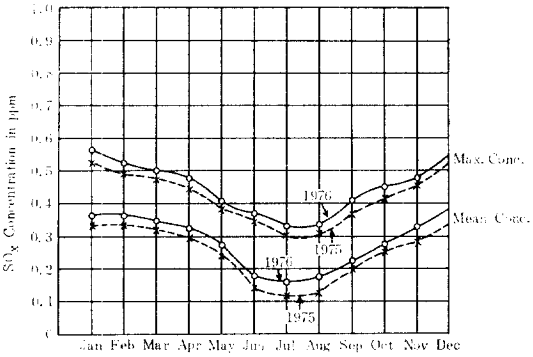


Fig. 4. The concentration of sulfur oxides in the atmosphere of Seoul, Korea

smog phenomenon is not severe in Seoul during winter because the solar radiation intensities are not significant and the relative humidities are not high in the winter season, and the diffusion of air contaminants is more rapid in the winter season due to the north wind. The solar radiation intensities are very high and the smog phenomenon occurs frequently during the summer season, but the pollutants would have been removed by the rain during the rainy season. Therefore, the chances of occurrence of smog phenomenon in Seoul are not very frequent.

Conclusions

The results of the photochemical reaction of sulfur oxide in air at a concentration of 1 to 20 ppm under the presence of nitrogen dioxide are summarized as follows;

1. When air contains NO_2, SO_2 and water particles, nitrosyl-sulfuric acid would be initially formed, caused by the photochemical reaction, and then the sulfuric acid would be produced as a result of decomposition of the nitrosyl-sulfuric acid by water.
2. The sulfuric acid formation rate increased with reaction time when the photochemical reaction proceeded at varied SO_2 concentrations under fixed NO_2 concentration. The principal reaction to produce the sulfuric acid took place over the period from two to four hours of reaction time and then the rate decreased after four hours.
3. The sulfuric acid formation rate increases with increase in both the concentrations of NO_2 and SO_2, respectively.
4. The sulfuric acid formation rate is faster at a foggy state than at the steam saturated conditions where water droplets are absent.
5. The air pollution condition with respect to SO_2 in Seoul, Korea has approached the standard condition of public nuisance and shown a tendency of increasing the SO_2 concentration annually.

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