

## Studies on Photochemical Reactions of Air Pollutants. XIV. Photooxidation of Sulfur Dioxide in Air by Various Air Pollutants

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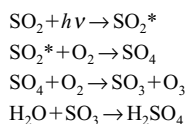
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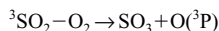
**Upon exposure to sunlight, or to artificial light at wavelengths longer than 290 nm, sulfur dioxide in air underwent oxidation to give sulfur trioxide in the presence of air pollutants such as biacetyl (2,3-butanedione), benzaldehyde and nitrogen dioxide, but not in their absence. Only nitrogen dioxide completely oxidized sulfur dioxide to sulfur trioxide.**

**Key words** sulfur dioxide; sulfur trioxide; nitrogen dioxide; biacetyl; benzaldehyde; photooxidation

The rates and mechanisms of the transformations of sulfur dioxide in sunlight-irradiated atmosphere are of interest, because sulfur dioxide emitted from the combustion of fossil fuels containing sulfur has caused severe smog episodes in London and elsewhere. Renzetti and Doyle<sup>1)</sup> found that in sulfur dioxide-hydrocarbon aerosol systems, the photooxidation of sulfur dioxide proceeds at the rate of 0.4% per minute. This is considerably higher than that observed by Johnstone and Coughanowr,<sup>2)</sup> but is consistent with the high sulfate content of the particulate matter in Los Angeles smog. Shirai *et al.*<sup>3)</sup> have reported that the rate constant of oxidation of sulfur dioxide to sulfur trioxide in air having 70.7 mg/l humidity was  $1.91 \times 10^{-3} \text{ s}^{-1}$  under irradiation with a mercury lamp through glass. According to Blacet,<sup>4)</sup> the mechanism of the photooxidation of sulfur dioxide may be represented by:



This process provides a route through which ozone may be produced as a by-product of the photochemical reaction. Calvert and co-workers<sup>5,6)</sup> examined the photo-excited states of sulfur dioxide in air and proposed that the oxidation to sulfur trioxide in air may proceed as follows:



This hypothesis, like the Blacet mechanism, has not been tested adequately as yet.

In connection with these investigations, we are interested in whether or not sulfur trioxide is produced when sulfur dioxide in air is irradiated with a xenon lamp (cut-off below 290 nm) or sunlight in the absence and presence of air pollutants such as biacetyl, benzaldehyde and nitrogen dioxide. The former two pollutants were observed in smog chamber experiments,<sup>7-9)</sup> and are known to be epoxidizing agents that can convert aldrin photochemically to dieldrin.<sup>10-12)</sup>

We wish to report herein the oxidation of sulfur dioxide in air in the presence of air pollutants and the product distribution in the photochemical reaction.

### Experimental

**Materials** Sulfur dioxide (99.98%) and nitrogen monoxide (99%) were purchased from Atheson Gas Products Inc. and Nippon Sanso Co. Ltd., respectively. Biacetyl and benzaldehyde were supplied by Wako Pure Chemi-

cals Industries Ltd. Other chemicals used in the experiments were supplied by Wako Pure Chemicals Industries Ltd. or Tokyo Kasei Kogyo Co. Ltd., and were purified before use, if necessary.

**Analytical Equipment** Gas liquid chromatography (GLC) was carried out with a Shimadzu 9A gas chromatograph equipped with a flame ionization detector. A coiled glass column (3 mm i.d.  $\times$  1.1 m) packed with 1.5% Silicone SE-30 on Chromosorb WAW-DMCS (60–80 mesh) was employed. Other conditions were as shown in Table 1.

High-performance liquid chromatography (HPLC) was done with a GL Sciences PU 614 equipped with a ultraviolet-visible detector and a 20  $\mu$ l sample loop. A stainless steel column (4.6 mm i.d.  $\times$  150 mm) packed with ODS was used. Other conditions were also as shown in Table 1.

Ion chromatography (IC) was done with a Metrohm 761 Compact IC equipped with a Shodex IC SI-90 4E column (4.0 mm i.d.  $\times$  150 mm), a conductivity detector and a 20  $\mu$ l sample loop. Other conditions were as shown in Table 1.

**Irradiation of Sulfur Dioxide in the Presence of Biacetyl, Benzaldehyde or Nitrogen Dioxide in Air** One milliliter of sulfur dioxide was taken in a 180 ml Pyrex reaction vessel filled with air having *ca.* 50% humidity, and 44.6  $\mu$ mol (1000  $\mu$ l gas in the standard state) of biacetyl, benzaldehyde or nitrogen monoxide (which was readily oxidized to nitrogen dioxide with air at this concentration) was injected into the vessel. Then, the mixture was irradiated for 0.5, 1.0, 2.0 or 3.0 h with a xenon lamp (300 W, ozoneless type, Ushio Inc.). After irradiation, the reaction mixture was treated as mentioned below and used for the analysis of the compounds shown in Table 1. In order to determine the initial quantity of sulfur dioxide or nitrogen dioxide employed, the procedure described below was employed.

Similar mixtures were exposed to sunlight (August 4, 2003) for 3 h on the campus of Josai University. After sunlight exposure, the reaction mixture was treated as described below and subjected to analysis of sulfur dioxide and sulfur trioxide only.

**Analysis** Procedure (1): Ten milliliters of 0.1 M hydrochloric acid containing *o*-phenylenediamine ( $4.5 \times 10^{-2}$  mol) solution was injected into the reaction vessel, and then shaken. Five milliliters of the resulting solution was taken into a test tube, and heated at  $80 \pm 1$  °C for 30 min. After the solution had cooled, 5.0 ml of benzene was added to it, and the mixture was shaken. Two microliters of the resulting benzene solution was employed for GLC analysis.

Procedure (2): Ten milliliters of ethanol was injected into the reaction vessel, and then shaken. Twenty microliters of the resulting solution was used for HPLC analysis.

On the other hand, 0.5 ml of the resulting solution was added to 1.0 ml of 1.8 M sulfuric acid containing 4-nitrophenylhydrazine ( $1.0 \times 10^{-2}$  mol) solution in a test tube, followed by heating at  $50 \pm 1$  °C for 5 min. After the solution had cooled, 4.0 ml of distilled water and 5.0 ml of ethyl acetate were added to it, and the mixture was shaken. Twenty microliters of the resulting ethyl acetate solution was used for HPLC analysis.

Procedure (3): Into the reaction vessel, 200  $\mu$ l of ethanol was injected and allowed to stand for 5 min at room temperature, followed by injection of 10 ml of  $9.0 \times 10^{-3}$  M sodium carbonate solution. The mixture was shaken, and the resulting solution was transferred to a volumetric flask, followed by washing of the vessel with 20 ml of distilled water three times. The volume was adjusted to 100 ml with distilled water. Twenty microliters of the resulting solution was utilized for IC analysis.

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Table 1. Analytical Conditions of GLC, HPLC and IC

	GLC	HPLC	IC
Compound	Biacetyl (as quinoxaline) <sup>a)</sup>	Benzoic acid <sup>b)</sup> Benzaldehyde (as 4-nitrophenylhydrazone) <sup>c)</sup>	Sulfur dioxide (as sulfite ion) <sup>d)</sup> Sulfur trioxide (as sulfate ion) Nitrogen oxides (as nitrite ion and nitrate ion) Formic acid <sup>e)</sup> Acetic acid
Column temp.	130 °C	20 °C	20 °C
Eluent	Helium	Acetonitrile/25 mM acetate buffer=2/3 (v/v) <sup>b)</sup> Acetic acid/H <sub>2</sub> O=7/3 (v/v) <sup>c)</sup>	1.7 mM NaHCO <sub>3</sub> and 1.9 mM Na <sub>2</sub> CO <sub>3</sub> / Acetone=100/3.5 (v/v)
Flow rate	30 ml/min	1.0 ml/min	0.80 ml/min
Injection volume	2.0 μl	20 μl	20 μl
Wavelength	—	240 nm <sup>b)</sup> 450 nm <sup>c)</sup>	—

a) Residual biacetyl in the reaction vessel reacted with *o*-phenylenediamine in dilute hydrochloric acid to give quinoxaline. This was extracted with benzene, and the solution was analyzed by GLC. This method was modified as described in the previous paper.<sup>7)</sup> b) As benzoic acid could not be determined by IC owing to the occurrence of tailing, HPLC was used. c) Benzaldehyde generated an adduct with sulfur dioxide. Accordingly, residual benzaldehyde in the reaction vessel was allowed to react with 4-nitrophenylhydrazine in dilute sulfuric acid to afford the hydrazone. This was extracted with ethyl acetate, and the solution was analyzed by HPLC. If 2,4-dinitrophenylhydrazine was used instead of 4-nitrophenylhydrazine, the hydrazone produced was not completely extracted into various solvents. d) Sulfur dioxide treated with dilute alkaline solution tended to give not sulfite ion, but sulfate ion, so ethanol was used as an anti-oxidant. e) Under the analytical conditions of IC, the peaks of formic acid and pyruvic acid could not be clearly distinguished, so the following procedures were adopted: in one, formic acid in the reaction vessel was reduced with magnesium in dilute hydrochloric acid to give formaldehyde, which was converted to the corresponding hydrazone using 2,4-dinitrophenylhydrazine; in the second, some of the carbonyl compounds in the reaction vessel were similarly converted into the corresponding hydrazones; in the third, the hydrazones were separated by thin layer chromatography (TLC) using silanized Kieselgel 60.

Procedure (4): Before irradiation, 10 ml of 0.3 w/v% hydrogen peroxide solution was injected into the vessel containing only sulfur dioxide or sulfur dioxide and nitrogen dioxide in air, and the mixture was allowed to stand for 1 h at room temperature. The resulting solution was transferred to a volumetric flask, followed by washing of the vessel with 20 ml of distilled water three times. The volume was adjusted to 100 ml with distilled water. Twenty microliters of the resulting solution was utilized for IC analysis.

## Results and Discussion

Figure 1 shows a plot of sulfur dioxide consumption *versus* irradiation time. When sulfur dioxide alone was irradiated in air with a xenon lamp through a Pyrex filter (cut-off below 290 nm), no change occurred. As shown in Table 2, sunlight exposure of sulfur dioxide in air without air pollutants also produced no change. In other words, sulfur dioxide itself was found to be photochemically inactive, in contrast to the results obtained by Renzetti and Doyle,<sup>1)</sup> and Shirai *et al.*<sup>3)</sup> The difference might be based on the analytical procedures employed, because sulfur dioxide is liable to oxidation in alkaline solution. To prevent such oxidation, we chose ethanol from among many solvents miscible with water as an anti-oxidant.

We then examined whether or not sulfur trioxide was produced when sulfur dioxide was irradiated with the same lamp in the presence of air pollutants such as biacetyl, benzaldehyde and nitrogen dioxide in air, and we examined the product distribution in order to clarify the photochemical reactions involved. Figure 2 shows plots of sulfur dioxide and biacetyl consumption and concomitant sulfur trioxide, acetic acid and formic acid formation *versus* irradiation time. Apparently biacetyl could act as a photochemical oxidizing agent in air. The oxidation of sulfur dioxide to sulfur trioxide ceased after 2 h irradiation, when biacetyl had almost disappeared. This may imply that biacetyl is consumed to generate the oxidant converting sulfur dioxide to sulfur trioxide. For example, the oxidant may be produced as follows.<sup>13)</sup> Sawaki<sup>13)</sup> reported that photochemical reaction of  $\alpha$ -diketones such as biacetyl in benzene in the presence of O<sub>2</sub> gave the peroxy radical, which oxidized olefins to the corresponding epox-

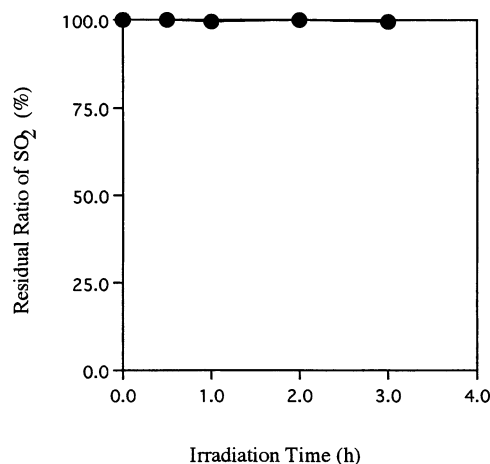


Fig. 1. Irradiation of SO<sub>2</sub> in Air in the Absence of Air Pollutants SO<sub>2</sub> consumption (●) *versus* irradiation time.

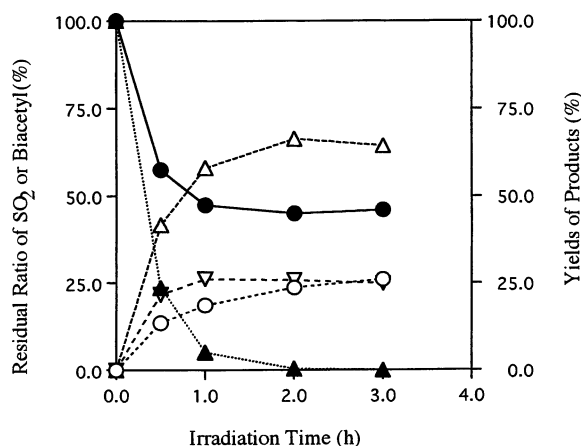


Fig. 2. Irradiation of SO<sub>2</sub> in Air in the Presence of Biacetyl SO<sub>2</sub> (●) and biacetyl (▲) consumption and concomitant SO<sub>3</sub> (○), acetic acid (△) and formic acid (▽) formation *versus* irradiation time.

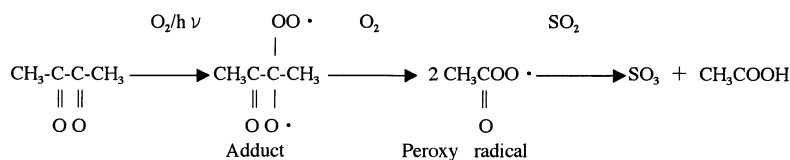


Chart 1

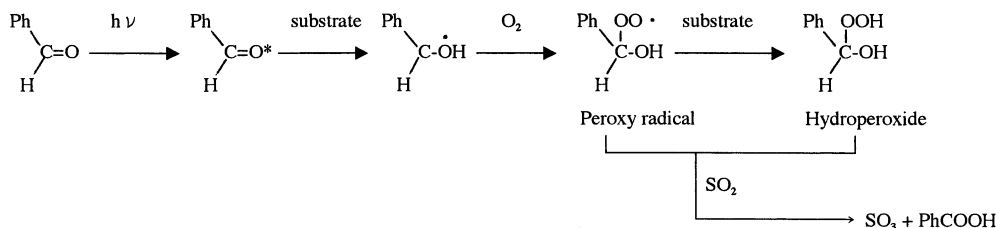
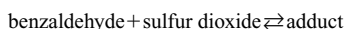


Chart 2

ides. Thus, sulfur dioxide might be oxidized with peroxy radical to sulfur trioxide, while the radical is converted into acetic acid, as shown in Chart 1. The quantity of sulfur dioxide consumed did not correspond to that of sulfur trioxide produced, but the reason for this is not clear. On the other hand, biacetyl itself decomposes to acetic acid and formic acid, but the amount of formic acid formed has not been clarified.

Figure 3 shows plots of sulfur dioxide and benzaldehyde consumption and concomitant sulfur trioxide and benzoic acid formation *versus* irradiation time. Benzaldehyde was also found to be a photochemical oxidizing agent in air. After only 0.5 h irradiation, the consumption of sulfur dioxide no longer proceeded even though benzaldehyde remained, while the formation of sulfur trioxide was proportional to sulfur dioxide consumed. This might be related to the following two facts. One, benzaldehyde itself disappeared rapidly at 81% and 88% with 3 h standing in air and with 3 h irradiation in air to give benzoic acid (44% and 50% yield based on benzaldehyde disappeared), respectively. It was found that benzaldehyde in air was liable to undergo oxidation. The other, when benzaldehyde was brought into contact with sulfur dioxide in air, the mixture generated a red adduct which might be moderately stable (not chromatographically separable). Benzaldehyde in the presence of sulfur dioxide disappeared at 51% with 3 h standing in air to afford benzoic acid (35% yield based on benzaldehyde disappeared). Then, benzaldehyde in the adduct appeared to resist oxidation. In other words, sulfur dioxide was found to prevent benzaldehyde from oxidizing.

Anyway, it was postulated that an equilibrium between benzaldehyde and sulfur dioxide was present as follows:



The carbonyl group in the adduct might not be available for excitation under irradiation. Judging from Fig. 1, benzaldehyde dissociated gradually from the adduct might be more immediately oxidized than sulfur dioxide after sulfur dioxide was consumed by half.

Generally, carbonyl compounds act as triplet-state photosensitizers,<sup>14–20</sup> abstracting an H atom from a substrate to form a radical.<sup>15,16,21–26</sup> If the electron of the radical is local-

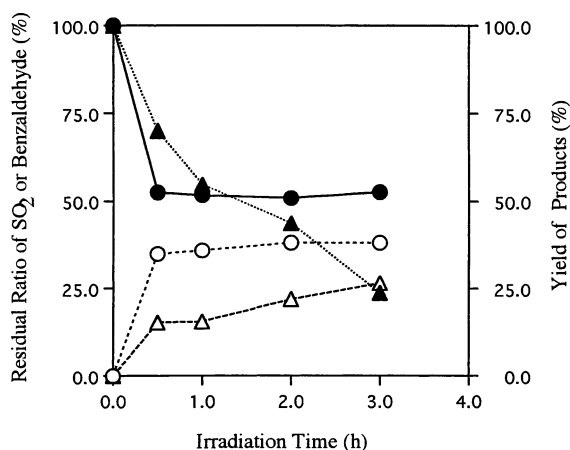
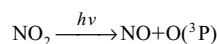


Fig. 3. Irradiation of SO<sub>2</sub> in Air in the Presence of Benzaldehyde

SO<sub>2</sub> (●) and benzaldehyde (▲) consumption and concomitant SO<sub>3</sub> (○) and benzoic acid (△) formation *versus* irradiation time.

ized on the carbonyl carbon atom, the radical is liable to react with oxygen to produce a peroxy radical, followed by H-abstraction to give a hydroperoxide.<sup>25,26</sup> These active species, namely peroxy radical and hydroperoxide, could have epoxidizing ability.<sup>27–29</sup> When the carbonyl compound is benzaldehyde, the reaction sequence is expected to be as shown in Chart 2, *i.e.*, the oxidation of sulfur dioxide proceeds through reaction with peroxy radical or hydroperoxide derived from benzaldehyde to afford sulfur trioxide and benzoic acid.

Figure 4 shows plots of sulfur dioxide and nitrogen dioxide consumption and concomitant sulfur trioxide formation *versus* irradiation time. It has been established<sup>30</sup> that the primary photo process of nitrogen dioxide at wavelengths of less than *ca.* 398 nm is dissociation, with a primary quantum yield of approximately unity:



The resulting oxygen atom O(<sup>3</sup>P) acts directly as an oxidizing agent, converting sulfur dioxide to sulfur trioxide. We next examined what proportion of sulfur dioxide was turned into sulfur trioxide. After 2 h irradiation, all of the sulfur

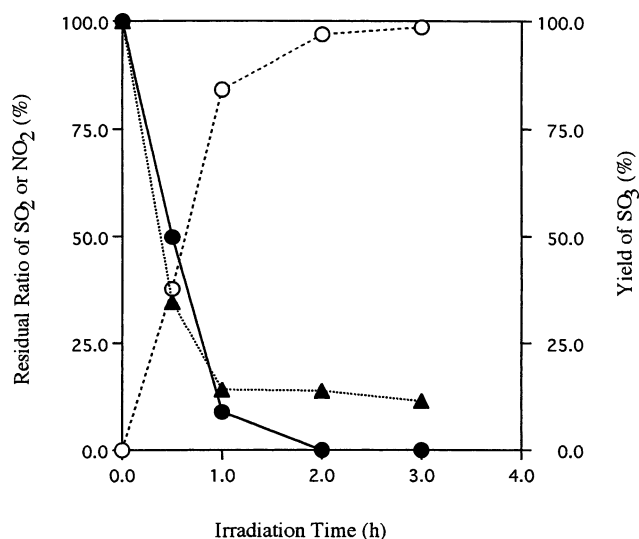


Fig. 4. Irradiation of SO<sub>2</sub> in Air in the Presence of NO<sub>2</sub>  
SO<sub>2</sub> (●) and NO<sub>2</sub> (▲) consumption and concomitant SO<sub>3</sub> (○) formation versus irradiation time.

Table 2. Photooxidation of SO<sub>2</sub> in Air in the Absence and Presence of Air Pollutants under Sunlight Exposure<sup>a)</sup>

Reactants	Product (yield) <sup>b)</sup>
SO <sub>2</sub> only	SO <sub>3</sub> (0%)
SO <sub>2</sub> +biacetyl	SO <sub>3</sub> (41%)
SO <sub>2</sub> +benzaldehyde	SO <sub>3</sub> (60%)
SO <sub>2</sub> +NO <sub>2</sub>	SO <sub>3</sub> (95%)

<sup>a)</sup> SO<sub>2</sub>, 44.6 μmol; air pollutant, 44.6 μmol; exposure time, 3 h. <sup>b)</sup> Yields are [the molar amount of SO<sub>3</sub> formed/the molar amount of SO<sub>2</sub> used]×100.

dioxide had disappeared, with formation of a corresponding amount of sulfur trioxide. In other words, sulfur dioxide was quantitatively oxidized to sulfur trioxide under irradiation in air in the presence of nitrogen dioxide, though the fate of nitrogen dioxide was not examined here.

The results show that nitrogen dioxide oxidized sulfur dioxide to sulfur trioxide more efficiently than did the other pollutants.

From an environmental viewpoint, we investigated whether or not sulfur trioxide was produced when sulfur dioxide was exposed to sunlight instead of the xenon lamp in the absence or presence of biacetyl, benzaldehyde and nitrogen dioxide. The results are shown in Table 2.

There was no apparent difference in effectiveness between xenon lamp irradiation and sunlight exposure.

In conclusion, it was found that sulfur dioxide was oxidized to sulfur trioxide in the presence of air pollutants which could produce active species as oxidants, but not in their absence. It would be desirable to examine the photochemical activities of other major air pollutants.

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