



## Environmental chamber study of the photochemical reaction of ethyl methyl sulfide and NO<sub>x</sub>

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### Abstract

A series of experiments were conducted in a self-made smog chamber at  $(300 \pm 1)$  K and  $1.01 \times 10^5$  Pa to simulate the photochemical reaction of ethyl methyl sulfide (EMS) and NO<sub>x</sub>. The results showed that the higher the initial concentration of EMS, the more ozone was generated in the simulative reactions. It was found that the light intensity plays a very important role in the evaluation of ozone formation potential for EMS. The parameters of  $d(\text{O}_3\text{-NO})$  and IR (incremental reactivity) were used to quantify the potential of EMS on ozone formation. The obtained maximum IR values in this article for the five simulative reactions were  $1.55 \times 10^{-2}$ ,  $0.99 \times 10^{-2}$ ,  $1.36 \times 10^{-2}$ ,  $2.47 \times 10^{-2}$ , and  $1.65 \times 10^{-2}$ , respectively. A comparison between the results we obtained here and the results we obtained previously for di-tert-butyl peroxide and acetylene showed that the potential reactivity of EMS on ozone formation was at a relatively low level.

**Key words:** smog chamber; photochemical reaction; ethyl methyl sulfide; incremental reactivity

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### Introduction

In the troposphere, volatile organic compounds (VOCs) and oxides of nitrogen (NO<sub>x</sub>) are the main reactants in the photochemical reactions that produce ozone and other oxidizing compounds (hydrogen peroxide, peroxy acetyl nitrate or PAN) in the presence of sunlight and this is an important air-quality problem all over the world. Moreover, it is well recognized that individual VOCs differ significantly in both the rates and products of their oxidation reactions (Atkinson, 2000). These differences will affect the extent to which the reactions promote ozone formation (Altshuller and Bufalini, 1971; Darnall *et al.*, 1976; Carter and Atkinson, 1987; Carter *et al.*, 1994). In order to develop effective and efficient strategies to reduce the formation of ozone, the ozone-formation potential of VOC must be considered.

As one important kind of VOC, a large amount of volatile sulfur compounds are emitted into the atmosphere by natural and anthropogenic activities. Among them, natural and anthropogenic emissions of COS, H<sub>2</sub>S and dimethyl sulfide (DMS) play major roles (Mu *et al.*, 2002), but other species including thioether should also be taken into account. Thioether is widely used in various industries. Aryl, alkenyl and alkyl thioethers are important synthetic reagents and intermediates in organic synthesis.

They have been employed in the synthesis of novel biologically active compounds (Morris and Stanislaw, 1993), polymer materials (Masumura *et al.*, 2001) and used as extracting reagents (Elmroth *et al.*, 1992). Because of the frequent unpleasant smells associated with them even at very low levels, thioethers are also mixed into Liquefied Petroleum Gas (LPG) and fuel cell as leakage sensor odorants (Imamura *et al.*, 2005). Alkyl thioethers which can be found in garlic are synthesized and used as forage additives. These uses may result in their potential release into the atmosphere.

The photochemical reactivities of different types of VOCs have been investigated using different methods (Carter and Atkinson, 1987; Yin *et al.*, 1990; Carter *et al.*, 1995; Hurley *et al.*, 1998; Kelly and Chang, 1999; Khan and Chang, 1999; Martien *et al.*, 2003). Wang *et al.* (1989) simply simulated the reactions of propylene and NO<sub>x</sub> with a smog chamber equipped with Fourier Transform Infrared Spectrometer. Recently, our group simulated the photooxidation of NO<sub>x</sub> with acetylene (Du *et al.*, 2007a) and di-tert-butyl peroxide (Du *et al.*, 2007b).

In this work, using the simulative reaction apparatus of our self-made photochemical smog chamber (Du *et al.*, 2007a, 2007b), combined with some analytical instruments including O<sub>3</sub> analyzer and NO<sub>x</sub> analyzer, simulative experiments for the photochemical processes of ozone formation were conducted in the presence of ethyl methyl sulfide

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(EMS) and  $\text{NO}_x$ . The results were used to discuss the potential contribution of EMS to ozone formation.

## 1 Experiments

### 1.1 Reagent and equipments

Ethyl methyl sulfide was purchased from Alfa Aesar.  $\text{NO}_2$  in purified  $\text{N}_2$  was supplied by Beijing Zhaoge Special Gases Science and Technology Co., Ltd., with a mixing ratio about  $99.8 \times 10^{-6}$ .  $\text{N}_2$  and  $\text{O}_2$  were purchased from Beijing AP Beifen Gases Industry Co., Ltd., in purity of 99.999% and 99.995%, respectively.

The smog chamber used here is similar to the chamber we reported in previous publications (Du *et al.*, 2007a, 2007b) with some improvements. In a typical experiment, the reactor used is a 100-L bag which is made of 0.10 mm FEP Teflon film. With perfect transmittance of ultraviolet light, good endurance to chemicals and little absorption of reactants, FEP Teflon film is excellent for making the reactor. At the two ends of the reactor, there is an inlet and an outlet made of Teflon material facilitating the introduction of reactants and sampling. The bag is housed in a light-tight box made of iron. The interlayer of the box is filled with PS (Polystyrene) material to maintain the temperature in the box. The temperature in the chamber can be controlled accurately from room temperature to 350 K. There are six lamp-holders on the interior wall of the box used for fixing blacklight lamps. The blacklight lamps (Model F40T8BL, Beijing Light Research Institute, China) provide ultraviolet light with an emission wavelength range of 290–430 nm, which is in good agreement with the distribution of real tropospheric sunlight in ultraviolet region. The power of the lamp is 40 W each. The interior wall of the box is covered with aluminum foil to strengthen the reflection of ultraviolet light and to improve the light efficiency. During the experiment, the box is closed.

Ozone analyzer (Model 49C, Thermo Electron Corporation, USA) was used for analyzing the ozone concentration in the reactor. The  $\text{NO}_x$  concentration was monitored with the Model 42C- $\text{NO}_x$  analyzer (Thermo Electron Corporation, USA). The concentration of EMS was calculated from the amount of organics introduced and the total volume of the reactor.

In the experiment, mixture of  $\text{N}_2$  and  $\text{O}_2$  is used as bath gas. Purified  $\text{N}_2$  and  $\text{O}_2$  are introduced into the reactor simultaneously through two calibrated mass flow controllers (Model D07-7B/ZM, Beijing Sevenstar Electronics Co., Ltd., China). The mass flow controllers are adjusted to control the flux of  $\text{N}_2$  and  $\text{O}_2$  at a ratio of 80/20, so that the mixture is similar to real purified air in composition. The introduction of  $\text{NO}_2$  was controlled by a piping type flowmeter (Model LZB-2, Yuyao Yinhuan Flowmeter Co., Ltd., China).

### 1.2 Experimental procedure

As we reported in the previous articles (Du *et al.*, 2007a, 2007b), at first the wall decays of ozone and  $\text{NO}_2$ , the background ozone formation in bath gas irradiated

by ultraviolet lamps and the effective intensity of the simulative ultraviolet light source were measured to test the reactor and instruments.

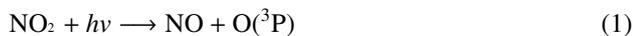
The reactor was purged with purified  $\text{N}_2$  for several times until there were no detectable ozone and  $\text{NO}_x$ . After the residual gas was pumped out, 100 L of the bath gas composed of  $\text{N}_2$  and  $\text{O}_2$  was introduced into the reactor. Then,  $\text{NO}_2$  was introduced into the reactor through the piping type flowmeter. The concentration of  $\text{NO}_2$  in the reactor was controlled by adjusting the flow rate of  $\text{NO}_2$  and introducing time to be about  $1.97 \times 10^{12}$  molecule/ $\text{cm}^3$ , which was for the range of observations from  $0.42 \times 10^{14}$  to  $2.14 \times 10^{14}$  molecule/ $\text{cm}^3$  for the photochemical pollution in cities, China (An *et al.*, 1999). The reactor was shaken fiercely to mix homogeneously after the reactor was maintained in the dark for 30 min without any activities. After that, a known amount of EMS was injected into the reactor with a syringe through the inlet on the reactor. The reactor was shaken and maintained in the dark for 30 min again. Then the concentration of  $\text{NO}_x$  in the reactor was measured. After that, the chamber was closed and the lamps were switched on for ultraviolet irradiation. At the same time, the time was recorded. During the experiment, the concentrations of  $\text{NO}_x$  and  $\text{O}_3$  were measured and recorded every 15 min. All the experiments were conducted at  $(300 \pm 1)$  K and  $1.01 \times 10^5$  Pa and lasted for 4 h.

In this study, the chamber used was different from the one we reported in previous articles (Du *et al.*, 2007a, 2007b), and the basic features of the apparatus and associated results also changed. The surface area/volume ratio of the new reactor is  $14.4 \text{ m}^{-1}$ , lower than that of the old reactor ( $17.1 \text{ m}^{-1}$ ). Correspondingly, the wall decays of ozone and  $\text{NO}_2$  are also lower than before, from  $5.80 \times 10^{-6}$  to  $5.20 \times 10^{-6} \text{ s}^{-1}$  and from  $2.41 \times 10^{-6}$  to  $2.26 \times 10^{-6} \text{ s}^{-1}$ , respectively. In this simulative experiment, both  $\text{NO}_2$  and ozone wall decay are very small and can be neglected.

In the experiments of the background ozone formation in bath gas irradiated by ultraviolet lamps, ozone with maximum concentrations of  $1.15 \times 10^{11}$  and  $1.62 \times 10^{11}$  molecule/ $\text{cm}^3$  are generated in 8 h under the irradiation of two and four lamps, respectively. In contrast, in the smog chamber used before (Du *et al.*, 2007a, 2007b), the maximum ozone concentration in 8 h under irradiation of two lamps is  $2.92 \times 10^{11}$  molecule/ $\text{cm}^3$ , higher than the result we obtained here. This is because that the bath gas used here is the mixture of purified  $\text{N}_2$  and  $\text{O}_2$  and the bath used before was purified air. Obviously, some trace components of the purified air would effect the background ozone formation under ultraviolet irradiation. On the other hand, organic compounds adsorbed on the inner Teflon wall might also contribute to the background ozone formation. When the lights are turned on, the organic compounds are heated and desorbed from the wall. Subsequent photochemical reactions of these compounds are likely responsible for ozone formation. The background ozone formation should be deducted in the subsequent experiments.

## 2 Results and discussion

The effective intensity is expressed by the rate constant of NO<sub>2</sub> photolysis in the bath gas in the unit of s<sup>-1</sup> (Wang *et al.*, 1989). The reactions involved are as the following:

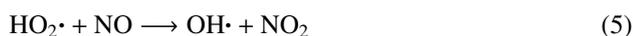


If there is no other species, Reactions (1)–(3) would result at a photostationary state between NO, NO<sub>2</sub>, and O<sub>3</sub> as Eq. (4).

$$k_1 = \frac{k_3 \times C_{\text{O}_3} \times C_{\text{NO}}}{C_{\text{NO}_2}} \quad (4)$$

where,  $k_1$  and  $k_3$  are the rate constants of Reactions (1) and (3). In our experiment, the experiments were conducted at (300 ± 1) K. At this temperature,  $k_3$  is 1.78 × 10<sup>-14</sup> cm<sup>3</sup>/(molecule·s) (Atkinson *et al.*, 2004). Thus according to Eq. (4), the effective light intensities used here can be calculated. The obtained effective light intensities are listed in Table 1. Compared with the result we reported before (0.65 × 10<sup>-3</sup> s<sup>-1</sup> for one lamp irradiation) (Du *et al.*, 2007a), the effective light intensities in this article are a little higher. Considering the basic features and the associated results, the apparatus here is comparable to the apparatus used before (Du *et al.*, 2007a, 2007b).

In the photochemical chamber, the photolysis of NO<sub>2</sub> leads to the formation of O(^3P) and its reactions with H<sub>2</sub>O and OH radicals are formed. OH radicals initiate the degradation reactions of VOCs and lead to the formation of HO<sub>2</sub>· and RO<sub>2</sub>·. The degradation reactions initiated by O(^3P) should also be considered under our experiment conditions. These radicals react with NO and converting NO to NO<sub>2</sub> (Reactions (5) and (6)).



Reactions (5) and (6) compete with Reaction (3), and at last would cause large amount of additional ozone formation.

The method in this article we used to evaluate the effect of EMS on ozone formation is based on the incremental reactivity approach. A known amount of EMS was added into the smog chamber, and the change in ozone concentration due to the additional organic compound was estimated.

The concentrations of O<sub>3</sub>, NO<sub>2</sub>, and NO under different simulation conditions were measured. The initial conditions and the results are listed in Table 2. The corresponding concentration-time profiles for the experiments under two lamps irradiation are showed in Fig. 1.

As shown in Table 2, it is found that the higher the initial concentration of NO<sub>2</sub> and EMS, the more ozone is generated in the reaction. The time needed for O<sub>3</sub> to reach its maximum concentration decreases with the increasing of the effective light intensity. As can be seen in Fig. 1, during the experiment, the concentration of NO<sub>2</sub> decreases with time while the concentration of ozone increase rapidly at the initial stage and decrease slowly after reaching the maximum value. At the beginning, the introduction of EMS into the chamber causes the rapid increase of the ozone concentration and complicated products might be generated. The products may also react with the radical intermediate even NO<sub>x</sub> and thus reduce the production of ozone. On the other hand, NO<sub>2</sub> can be efficiently consumed by the reaction with OH radical to form HNO<sub>3</sub>. This reaction also reduces the production of ozone. These reactions and the background ozone decay cause the concentration of ozone decrease slowly after reaching its maximum value. The maximum concentrations of ozone for EMS in this article were much lower than the results we reported before for acetylene and di-tert-butyl peroxide (Du *et al.*, 2007a, 2007b). For NO, it seems that at the beginning, a little amount of NO generated and during the experiment the concentration of NO decrease slowly. Even when O<sub>3</sub> reaches its maximum concentration, the concentration of

**Table 1** Photolysis of NO<sub>2</sub> under various light intensities

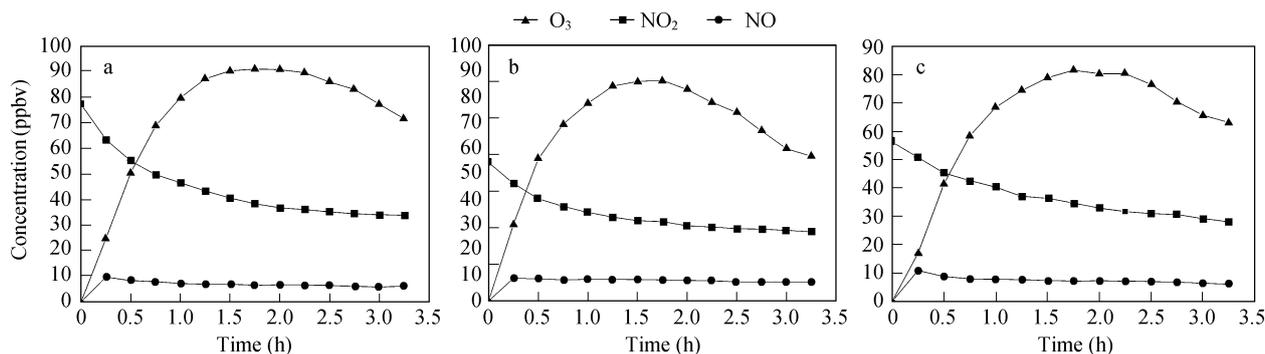
Experiment number	Lamp power (W)	C <sub>NO<sub>2</sub></sub> <sup>0</sup> (molecule/cm <sup>3</sup> )	C <sub>NO<sub>2</sub></sub> <sup>e</sup> (molecule/cm <sup>3</sup> )	C <sub>NO</sub> <sup>e</sup> (molecule/cm <sup>3</sup> )	C <sub>O<sub>3</sub></sub> <sup>e</sup> (molecule/cm <sup>3</sup> )	Effective light intensity (× 10 <sup>-3</sup> s <sup>-1</sup> )
1	40	1.53 × 10 <sup>12</sup>	1.16 × 10 <sup>12</sup>	3.10 × 10 <sup>11</sup>	1.70 × 10 <sup>11</sup>	0.79
2	80	1.48 × 10 <sup>12</sup>	1.03 × 10 <sup>12</sup>	3.67 × 10 <sup>11</sup>	2.63 × 10 <sup>11</sup>	1.64
3	160	1.45 × 10 <sup>12</sup>	0.93 × 10 <sup>12</sup>	4.87 × 10 <sup>11</sup>	3.32 × 10 <sup>11</sup>	3.07

C<sub>NO<sub>2</sub></sub><sup>0</sup>: initial concentration of NO<sub>2</sub>; C<sub>NO<sub>2</sub></sub><sup>e</sup>, C<sub>NO</sub><sup>e</sup>, C<sub>O<sub>3</sub></sub><sup>e</sup>: balanceable concentration of NO<sub>2</sub>, NO and O<sub>3</sub>, respectively.

**Table 2** Simulative experiments under different conditions

Experiment number	Lamp power (W)	C <sub>NO<sub>2</sub></sub> <sup>0</sup> (molecule/cm <sup>3</sup> )	C <sub>EMS</sub> <sup>0</sup> (molecule/cm <sup>3</sup> )	C <sub>O<sub>3</sub>-max</sub> (molecule/cm <sup>3</sup> )	t <sub>max</sub> (h)
4	80	1.90 × 10 <sup>12</sup>	1.34 × 10 <sup>14</sup>	2.24 × 10 <sup>12</sup>	1.75
5	80	1.86 × 10 <sup>12</sup>	2.67 × 10 <sup>14</sup>	2.97 × 10 <sup>12</sup>	1.75
6	80	1.38 × 10 <sup>12</sup>	1.34 × 10 <sup>14</sup>	2.00 × 10 <sup>12</sup>	1.75
7	160	1.77 × 10 <sup>12</sup>	1.34 × 10 <sup>14</sup>	3.63 × 10 <sup>12</sup>	1.50
8	160	1.61 × 10 <sup>12</sup>	2.67 × 10 <sup>14</sup>	4.45 × 10 <sup>12</sup>	1.00

C<sub>O<sub>3</sub>-max</sub>: maximum concentration of O<sub>3</sub> during the simulative experiments; C<sub>EMS</sub><sup>0</sup>: the initial concentration of ethyl methyl sulfide (EMS); t<sub>max</sub>: the time for O<sub>3</sub> to reach the maximum concentration from the beginning of the reaction.



**Fig. 1** Concentration-time profiles for  $O_3$ ,  $NO_2$ , and  $NO$  irradiated by two ultraviolet lamps under different initial concentrations of EMS and  $NO_2$ . (a)  $C_{EMS}^0$   $1.34 \times 10^{14}$  molecule/cm<sup>3</sup>,  $C_{NO_2}^0$   $1.90 \times 10^{12}$  molecule/cm<sup>3</sup>; (b)  $C_{EMS}^0$   $2.67 \times 10^{14}$  molecule/cm<sup>3</sup>,  $C_{NO_2}^0$   $1.86 \times 10^{12}$  molecule/cm<sup>3</sup>; (c)  $C_{EMS}^0$   $1.34 \times 10^{14}$  molecule/cm<sup>3</sup>,  $C_{NO_2}^0$   $1.38 \times 10^{12}$  molecule/cm<sup>3</sup>.

$NO$  remains a high value. Obviously, the  $NO$  decay caused by the reaction with  $HO_2\cdot$  and  $RO_2\cdot$ , which are from the degradation reactions of EMS, is small. This implies that the reactivity of EMS is at a relatively low level. As is shown in Table 2 that the time needed for  $O_3$  to reach its maximum concentration is less than 2 h in this system. The time needed decreases with the increase of light intensity from 1.75 h for two lamps irradiation to less than 1.5 h for four lamps irradiation. It is clear that the light irradiation plays an important role in the formation of ozone in this system, and this is in accordance with the observation of the real atmosphere. In the atmosphere, the photochemical smog usually appears in summer when the light intensity of the sunlight is strong.

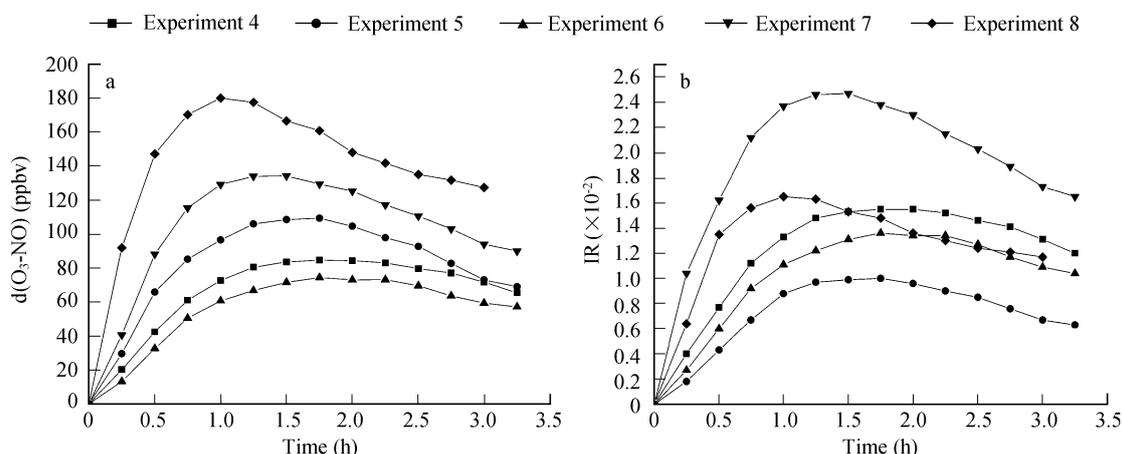
To quantify the effect of EMS on ozone formation, parameters proposed by Carter *et al.* (1987). The quantity ( $C_{O_3} - C_{NO}$ ), which is abbreviated as  $d(O_3-NO)$  in subsequence, is used to define the ozone-formation potential because it more effectively represents the chemical process leading to ozone formation than ozone alone. According to Reaction (3),  $O_3$  can be directly consumed by the reaction with  $NO$ , therefore, analysis of ozone formation should include changes in  $NO$ . Especially in this EMS-air- $NO_x$  system,  $NO$  remains a relatively high concentration during the reaction. Then the incremental reactivity (IR) of VOC

relative to  $d(O_3-NO)$  can be defined as Eq. (7).

$$IR_{VOC} = (d(O_3-NO)_{t,test} - d(O_3-NO)_{t,blank}) / C_{VOC_0} \quad (7)$$

where,  $d(O_3-NO)_{t,test}$  is the  $d(O_3-NO)$  measured at the time  $t$ , while  $d(O_3-NO)_{t,blank}$  is the corresponding  $d(O_3-NO)$  measured in the bath gas without any VOC. The obtained  $d(O_3-NO)$ -time profiles and corresponding IR-time profiles are shown in Fig. 2.

The incremental reactivity (IR) proposed by Carter and Atkinson (1987) is more useful under relatively high  $NO_x$  condition and the amount of VOC is depended on its reactivity. In this work, experiments under different concentrations of EMS are conducted and changes in the concentrations of  $NO_x$  and ozone are investigated. As shown in Fig. 2, with equal light irradiation and  $NO_2$  concentration, the  $d(O_3-NO)$  values increase with increasing of EMS concentration while the IR changes in an opposite direction. The results for experiment 4 and experiment 6 reveal that under equal other conditions, the reactive activity of EMS increased with the increasing of  $NO_2$  concentration in the system. Obviously, the concentration of  $NO_x$  in the real environment would effect the evaluation of the ozone formation potential for VOC. The maximum values of IR in our experiments 4, 5, 6, 7, and 8 were  $1.55 \times 10^{-2}$ ,  $0.99 \times 10^{-2}$ ,  $1.36 \times 10^{-2}$ ,  $2.47 \times 10^{-2}$ , and  $1.65 \times 10^{-2}$ , respectively. It is found that the maximum IR



**Fig. 2** Changes of  $d(O_3-NO)$  (a) and incremental reactivity (IR) (b) with time for experiments. The experiments 4–8 were defined as Tables 1 and 2.

values for experiments under strong ultraviolet irradiation were large. During the primary stage of the simulative reaction (from the beginning to the time when IR reaches its maximum value), the IR values obtained under four lamps irradiation were always larger than the values obtained under two lamps irradiation, even for experiment 8 in which the EMS concentration was high and the IR should present a small value (in fact that at the final stage, experiment 8 does exhibit small IR values). This clearly reveals that during the primary period, light irradiation plays a very important role in the evaluation of the ozone formation potential.

As we mentioned above, the IR depends on many factors, including the concentration of VOC and NO<sub>x</sub>, the intensity of the simulated light, the temperature and so on. The IR values obtained from different reactors for the same compound may differ greatly from each other and cannot be compared directly. Therefore, just a simple comparison between the results we obtained from similar apparatus is given here. Under two lamps irradiation (the effective light intensity was  $1.28 \times 10^{-3} \text{ s}^{-1}$ ), the maximum IR for acetylene with a concentration of  $1.75 \times 10^{14}$  molecule/cm<sup>3</sup> was  $2.68 \times 10^{-2}$  (Du *et al.*, 2007a). For di-*tert*-butyl peroxide, the maximum IR was  $3.78 \times 10^{-2}$  while the concentration of di-*tert*-butyl peroxide was  $1.50 \times 10^{14}$  molecule/cm<sup>3</sup> (Du *et al.*, 2007b). In this study, under irradiation of two lamps (the effective light intensity is  $1.64 \times 10^{-3} \text{ s}^{-1}$ ), the maximum IR value for EMS ( $C_{\text{EMS}}^0 = 1.34 \times 10^{14}$  molecule/cm<sup>3</sup>) was  $1.55 \times 10^{-2}$ . According to the rules we mentioned above and in previous publications (Du *et al.*, 2007a, 2007b) and considering the relatively low concentration of EMS in the atmosphere, obviously, EMS possesses a relatively low potential on the ozone formation in the atmosphere than acetylene and di-*tert*-butyl peroxide.

### 3 Conclusions

In this article, the influence of EMS emitted into the atmosphere on ozone formation was studied. Simulative photochemical reactions of EMS and NO<sub>x</sub> were conducted in a self-made smog chamber at  $(300 \pm 1) \text{ K}$  and  $1.01 \times 10^5 \text{ Pa}$ . The influences of EMS concentration, NO<sub>x</sub> concentration, and light intensity on the ozone formation were discussed. The parameters of d(O<sub>3</sub>-NO) and IR were used to illuminate the potential of EMS on ozone formation. The obtained maximum IR values in this study for the five simulative reactions were  $1.55 \times 10^{-2}$ ,  $0.99 \times 10^{-2}$ ,  $1.36 \times 10^{-2}$ ,  $2.47 \times 10^{-2}$  and  $1.65 \times 10^{-2}$ , respectively. Comparing with the results we obtained before for di-*tert*-butyl peroxide and acetylene, it could be concluded that the potential reactivity of EMS on ozone formation is at a relatively low level.

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