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中 華 民 國 91 年 7 月 31 日

行政院國家科學委員會專題研究計劃成果報告

都會區大氣中超細粒徑微粒之特性探討(III)

Characterization of Ultrafine Particles in Urban Atmosphere (III)

計畫編號: NSC 90-2320-B-002-174

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中文摘要

在周界大氣中，揮發性有機氣體的氧化反應會產生能夠凝結而形成二次有機氣膠的低揮發性有機化合物。排放自汽機車的反應性有機氣體是都會區大氣中二次有機氣膠前趨物質的主要來源，因此，本研究之主要目的為探討機車排氣經光化學反應後產生二次有機氣膠與反應性含氧物種之潛勢。

已濾除微粒之稀釋機車排氣經 UV 照射後會快速產生二次有機氣膠。經照射 2-3 小時後採樣袋內之微粒數目濃度達到尖峰。氣相反應性含氧物種則在照射 5-7 小時後出現高於初始濃度約十倍以上之尖峰濃度。此研究結果顯示在 UV 照射下，已事先濾除微粒之機車排氣具有甚高的二次有機氣膠及反應性含氧物種之形成潛勢。

關鍵詞：二次有機氣膠，機車排氣，反應性含氧物種，光化學反應。

Abstract

Oxidation of volatile organic gases in ambient air produces low-volatility compounds that condense to form secondary aerosol particles. In urban areas, the major sources of precursors for secondary organic aerosols (SOA) are the reactive organic gases (ROG) emitted from motor vehicles. This study aims at investigating the SOA and reactive oxygen species (ROS) formation potential of diluted motorcycle exhaust.

Irradiation of diluted motorcycle exhaust led to rapid formation of SOA. The particle number concentration in the bag peaked at 2-3 hours after UV irradiation. On the other hand, the gaseous ROS concentration increased with time to a peak at 5~7 hours. The peak concentration of gaseous ROS was about one-order of magnitude higher than the initial concentration in diluted motorcycle exhaust. The results suggest that the motorcycle exhaust with particles removed has a high potential to form ROS and SOA under UV irradiation.

Keywords: secondary organic aerosols (SOA), motorcycle exhaust, reactive oxygen species (ROS), photochemical reactions.

Introduction

Vehicular exhausts contain unburned hydrocarbons and NO that are the precursors of SOA and reactive chemicals such as organic peroxides and peroxy radicals. Oxidation of volatile organic compounds (VOCs) in the atmosphere generates low-volatility products that form new particles and thereby lead to increase in concentration of ambient aerosols. It is now recognized that reactive organic gases in vehicular emissions are an important contributor to secondary organic aerosols in ambient air (Kleindienst et al., 2002; Hurley et al., 2001). In motorcycle exhaust, there is a large mass fraction of SOA-associated hydrocarbon in gas phase such as aromatics including toluene, m,p-xylene, and

ethylbenzene.

While a direct differentiation between primary and secondary organic aerosols is difficult, a number of approaches have been developed to provide this distinction indirectly. Using the minimum ratio between particulate organic and black carbon, Castro et al. (1999) estimated that the secondary organic carbon could reach significant levels in summer months, constituting 50-65 % of the total particulate organic carbon in Birmingham, UK. In winter months, the percentage of secondary organic carbon calculated by this method dropped to around 17 %.

Highly reactive oxygen-containing species such as hydroxyl radical (OH), H_2O_2 , superoxide anion (O_2^-), singlet oxygen ($^1\text{O}_2$) are collectively described as ROS. In ambient air, photochemical reactions involving reactive organic gases are the major sources for ROS. Hung and Wang (2001) reported that concentrations of particulate ROS in ambient air are strongly associated with photochemical activities. There is a strong correlation between the concentrations of ambient ozone and ROS in submicron particles, especially in the ultrafine fraction (aerodynamic diameter $<0.18\ \mu\text{m}$) that are freshly produced by photochemical reactions and combustion processes in vehicular engines.

Motorcycle exhaust contains considerable levels of aromatics and aldehydes (Her et al., 1998), which have high potentials to form SOA and ROS. This study aims at examining the SOA and ROS formation potential of motorcycle exhaust under UV irradiation.

Results and Discussion

Figure 1 shows the typical time profiles of the gaseous ROS concentration and the total concentration of ROS in both the gas and particulate phases. The gaseous ROS concentration rose to one-order of magnitude higher than the initial concentration after 5~7 hours of irradiation. Subsequently, the ROS

formation rate became lower than the loss rate, and the measured ROS concentrations began to drop rapidly. Under the conditions of constant temperature and irradiation intensity, the decrease in ROS level may be caused by the depletion in reactive organic gases that take part in the ROS formation. In Figure 1, the difference in concentration between the total ROS (open circle) and the gaseous ROS (closed circle) is the concentration of the particulate ROS. A constant mole fraction of the total ROS was observed to be in the particle phase as the concentration of the total ROS built up. It can be concluded that the ROS in the gas phase were constantly in equilibrium with the ROS in the particle phase. The results of this experiment suggest that motorcycle exhausts have a high ROS formation potential.

Figure 2 illustrates the formation of SOA in diluted motorcycle exhaust under UV irradiation for different lengths of time. Because the motorcycle exhaust was collected with particles removed, very few particles were observed in the exhaust before irradiation. After exposing the exhaust to UV light for over 2 hours, the SOA formed rapidly and the number concentration reached a peak value of $6.4 \times 10^3\ \text{particles/cm}^3$. The number size distribution of SOA was unimodal with a mode diameter of $0.233\ \mu\text{m}$. After irradiating for 3.5 hours, the number concentration of particles decreased slightly and the mode diameter shifted to a larger size, about $0.385\ \mu\text{m}$.

After exposing to UV light for 6 hours, the particle number concentration decreased to a level one-order of magnitude lower than the peak concentration. Most particles have evolved out of the upper detection limit of the SMPS which is capable of measuring a diameter range of $0.014\sim0.723\ \mu\text{m}$. This can be verified by measurements of the gaseous ROS and the total ROS in both the gas and particle phases. After irradiation for more than 6~7 hours, the difference in concentration between the gaseous ROS and the total ROS showed that there was a significant amount of ROS in particulate

phase even though the particles cannot be detected (see Figure 1).

Concentration profiles of ROS, SOA, and NO₂ in the irradiated exhaust are shown in Figure 3. After irradiation for around 2 hours, the particulate matter was the first product to peak in number concentration. The concentration of the gaseous ROS that had a low initial level was just beginning to build up. NO₂ was still undetectable by a real time monitor, which has a detection limit of 0.02 ppm. Accumulation of NO₂ was observed after over 3 hours of irradiation when the particle number began to drop. Because NO₂ reacts with organic compounds to produce organonitrates, which have sufficiently low vapor pressures to condense on existing particles, the organic compounds play the role of a sink for NO₂. Once SOA was formed in the irradiated exhaust, NO₂ had no chance to accumulate. When the loss rate of SOA was higher than the production rate, the surfaces provided by SOA for adsorption of organonitrate compounds would decrease. As a result, the NO₂ accumulated and its concentration reached a peak after a significant decline in mass concentration of SOA.

Table 1 shows the ROS content per unit mass of fresh SOA was estimated from the mass concentrations of SOA calculated from the particle number size distributions. The estimated concentrations of particulate ROS from the three runs were in the range of 11~555 nmol/μg. Since particles may grow beyond the upper detection limit of SMPS, the calculated mass concentration of particles may be underestimated when the exhaust aged over 4.6 hours. As the particle mass concentration had been underestimated, the concentration of particulate ROS was overestimated. In addition, the ROS concentration in secondary organic aerosol decayed with time. The depletion of particulate ROS may be attributed to particle

aging. The smaller particles, especially ultrafine particles, are relatively fresh and contain a level of ROS higher than in larger particles.

Self-evaluation of Results

The goals of this project, which included a study of the SOA and ROS formation potential of irradiated motorcycle exhaust, were all completed. In addition, the concentration of ROS was determined for motorcycle exhaust particles of different size fractions.

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Table 1 Estimated concentrations of particulate ROS (nmol/ μg of particles) in diluted motorcycle exhaust after UV irradiation for different lengths of time.

Run #	Time, h	Particles, cm^{-3}	Mode dp, nm	ROS, nmol/ μg
I	1.4	2860	135.8	24.3
	2.9	2377	333.8	10.9
	4.5	833	532.8	16.3
II	1	529	35.1	555.0
	2.4	1704	181.1	50.4
	4.6	663	552.3	22.8
III	2.0	6413	232.9	41.0
	3.5	4813	385.4	15.2

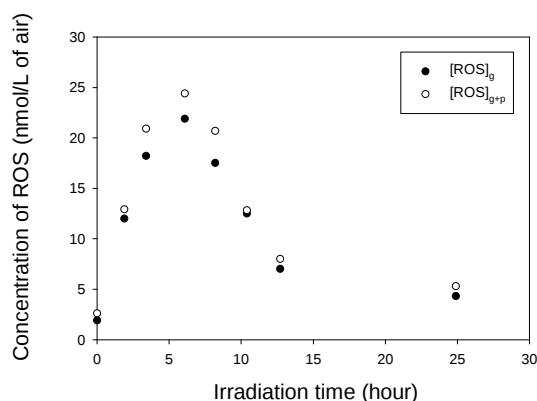


Figure 1 The time profiles of ROS concentrations in diluted motorcycle exhaust under UV irradiation (Run III).

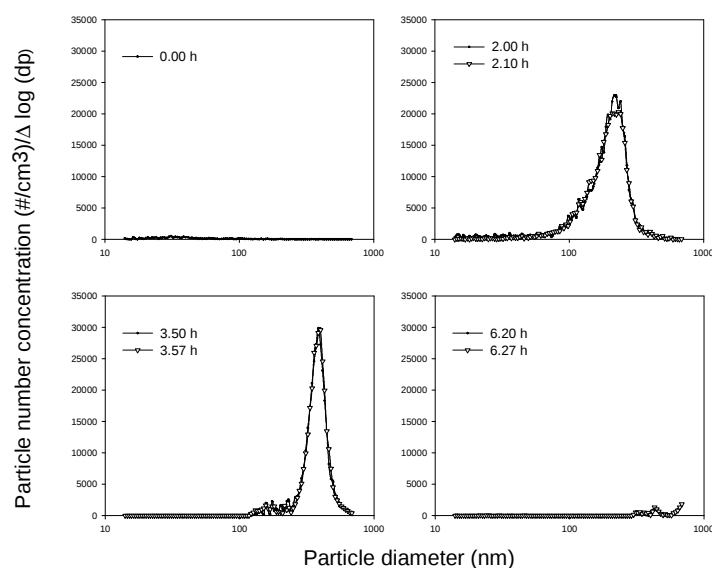


Figure 2 The particle number size distribution in diluted motorcycle exhaust measured at different irradiation times (Run III). After 5.3 hours of irradiation, the instrument began to underestimate the number of particles.

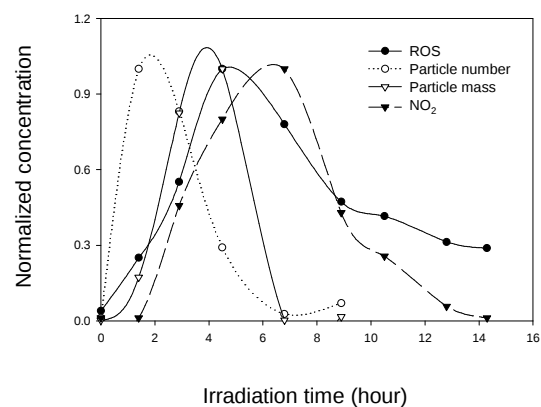


Figure 3 Normalized concentrations of gaseous ROS, particle number, particle mass, and nitrogen dioxide as functions of time during the UV irradiation of a diluted motorcycle exhaust. The concentrations were normalized by the maximum concentration measured for each pollutant (Run I). After 5.3 hours of irradiation, the instrument began to underestimate the number of