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Laboratory study on the OH-initiated degradation kinetics of dehydroabietic acid

Chengyue Lai, Yongchun Liu*, Jinzhu Ma, Qingxin Ma, and Hong He*

State Key Joint Laboratory of Environment Simulation and Pollution Control (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences), Beijing, 100085, China

Electronic Supplementary Information

1. Detailed experimental procedures for OH determination:

In this study, the measurements of salicylic acid degradation were both separately done from the DHAA degradation experiments and concurrently with the DHAA measurements. The OH concentration were calculated through the determination of the products of salicylic acid-OH reaction (2,3-dihydroxybenzonic acid and 2,5-dihydroxybenzonic acid), the principles are as follows. After a period of time for the reaction between salicylic acid and OH, the accumulative content of the products can be determined. It has been found that the production yields of 2,3-dihydroxybenzonic acid and 2,5-dihydroxybenzonic acid from the gas phase OH radical reaction with solid phase salicylic acid on filter are 52 % and 48 %, respectively [1]. Thus, the total mole number of OH which reacted with salicylic acid were calculated as the gas flow during this period was constant. Therefore, the near surface OH concentration can be calculated by the ratio of total mole number of OH with total gas flow.

In this study, the OH exposure results obtained concurrently with the DHAA

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*Corresponding authors. *E-mail address:* ycliu@rcees.ac.cn (Y. Liu), honghe@rcees.ac.cn (H. He)

measurements were used. Based on the method stated above, a series of repeated experiments (7 times) were carried out for each OH concentration, the results showed that the relative standard deviation (RSD) for OH concentrations were less than 10 %, which means that the repeatability of OH levels are acceptable. Three OH concentrations were obtained, they were $(2.05\pm0.06)\times10^7$ molecules·cm^{-3}, $(2.38\pm0.08)\times10^7$ molecules·cm^{-3} and $(2.99\pm0.10)\times10^7$ molecules·cm^{-3}, respectively. These three OH concentrations were used for the DHAA degradation experiments. In each experiment, we only need to set the ratio of N_2 to H_2O_2, total flow rate, temperature, and RH to get the desired OH concentration. By changing the ratio of N_2 to H_2O_2, the OH concentration in the reactor can be adjusted within 10 % of uncertainty.

2. Preparation procedures for the mixed samples:

DHAA-$(NH_4)_2SO_4$: 10.0 mL of DHAA solution (50.0 μg·mL^{-1} in methanol) was mixed with 10.0 mL of $(NH_4)_2SO_4$ aqueous solution (50.0 mg·mL^{-1}) and stirred uniformly for two hours. Subsequently, the solvent (methanol/water) was evaporated slowly using a rotary evaporator, and then the mixture was dried at room temperature in a flask.

DHAA/soot: 0.50 g soot was added to 50.0 mL of DHAA (10.0 μg·mL^{-1} in methanol). After stirring uniformly for two hours, the solvent (methanol) was evaporated slowly using a rotary evaporator and finally the mixture was dried at room temperature in a flask.

DHAA-$(NH_4)_2SO_4$/soot: 0.50 g soot was added to a mixed solution containing 10.0 mL of DHAA (50.0 μg·mL^{-1} in methanol) and 10.0 mL of $(NH_4)_2SO_4$ aqueous solution (50.0 mg·mL^{-1}), followed by stirring the mixture uniformly for two hours and then evaporating the solvent (methanol/water) to dryness. Finally the mixture was dried at room temperature in a flask.

3. Diffusion corrections:

In general, if experiments for the heterogeneous reaction are carried out under ambient pressure and on packed powder samples, both external (gaseous reactants from gas phase to the surface) and internal diffusions (from the surface layer to the underneath layers and into the pores of particles or films) need be corrected [2-4]. However, it is unnecessary to do both external and internal diffusion corrections in this study based on the following reasons.

Firstly, in this study, a particle phase reference salicylic acid (SA) was used to measure the near-surface OH concentration. The k_2 value for SA-OH reaction and DHAA-OH reaction were on the same order of magnitude, which means that OH concentration gradients should be very close in these two cases. Thus, we didn't do additional external diffusion corrections. On the other hand, the packed powder was used in our work, the internal diffusion of OH into the possible porous structure or underneath layers might be happened. As shown in Fig. S2 and Fig. S3, the surface of the salicylic acid, DHAA and the mixed samples are smooth, but not porous as supported by SEM images. For the heterogeneous reaction on packed powers, KML model is usually used to correct this kind of internal diffusion. In KML model, the probe depth of reactive gas can be expressed as a complex function of several parameters including bulk density (ρ_b), true density (ρ_t), pore size (r_p), porosity (θ), and particle diameter (d_p) of powder sample, diffusion constant (D_f) of reactive molecules, and the true uptake coefficient (γ_t). [2, 3]. Generally speaking, a small D_f and a large γ_t should result in a small probe depth and vice versa. However, KML model can be used only if the γ_t is less than 10^{-4}. This has been verified in our previous work [5]. Even for a reactive gas with γ_t of 7×10^{-3}, the reaction is found to occur on the surface layer [5]. According to the measured k_2, the estimated γ_t should be around unit. Therefore, it is impossible to use KML model to correct this kind of diffusion. We think the reaction between OH and DHAA should take place on the surface layer and the internal diffusion to the underneath layers is negligible. This assumption is reasonable because it has been widely accepted that oxidation of solid organic aerosols by radicals is a surface reaction [6].

References

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Table S1. Average size of DHAA mixed samples.

Sample	Average size (nm)
DHAA-AS	217.6 ± 95.7
DHAA/soot	52.1 ± 18.7
DHAA-AS/soot	89.8 ± 31.7

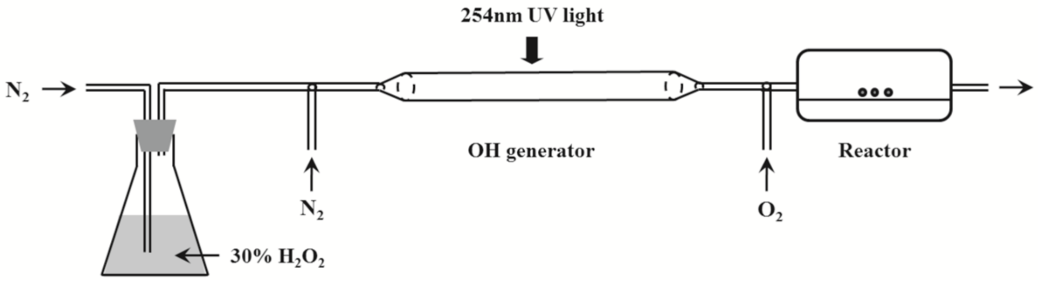

Fig. S1. Schematic diagram of the experimental set-up. The set-up consists of separated OH generation system and reaction system. The gas circuit system was divided into three parts, one of which was used to carry pure N_2 with water vapor corresponding to 40 % RH, another to carry pure O_2, a third carrying H_2O_2 with N_2 as the carrier gas.

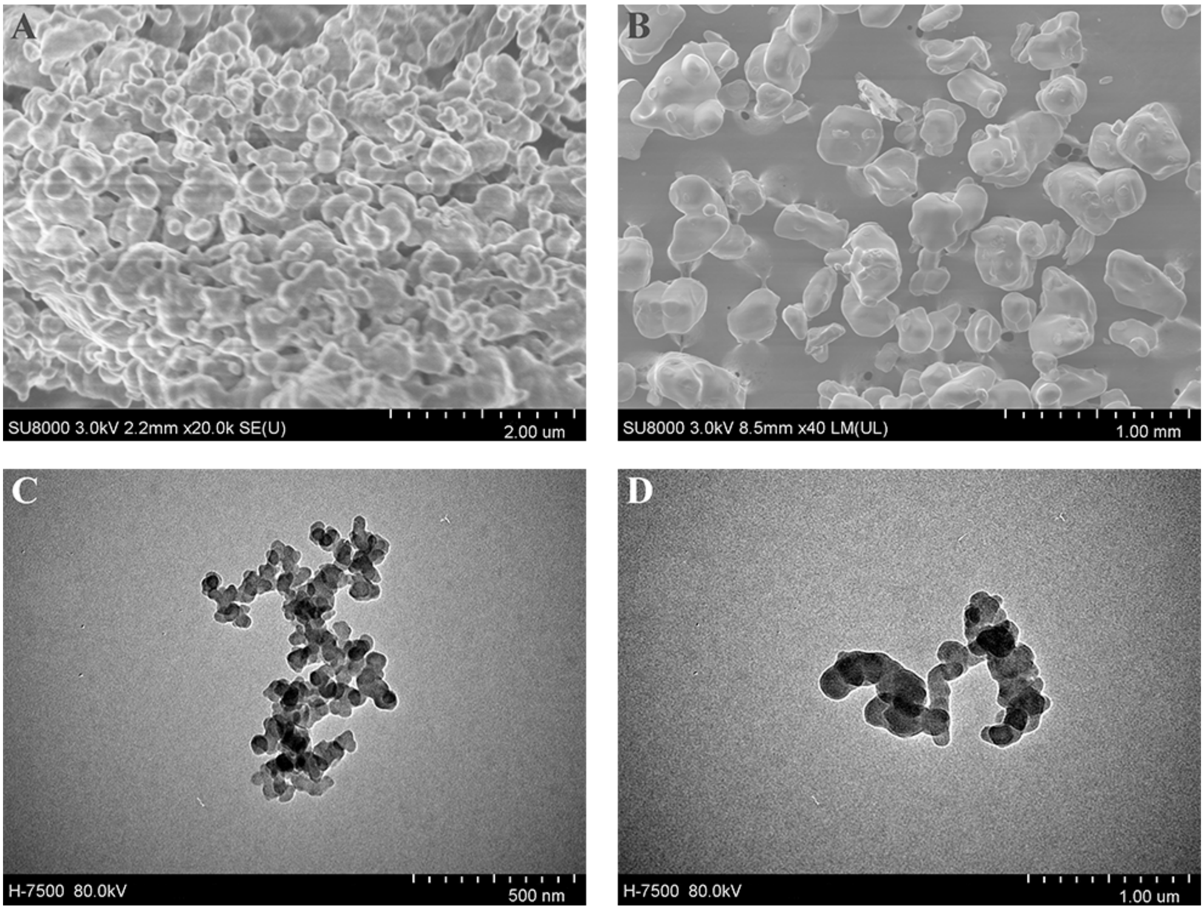

Fig. S2. Optical photomicrographs of the mixed samples. (A) DHAA-AS; (B) $(NH_4)_2SO_4$; (C) DHAA/soot; (D) DHAA-AS/soot.

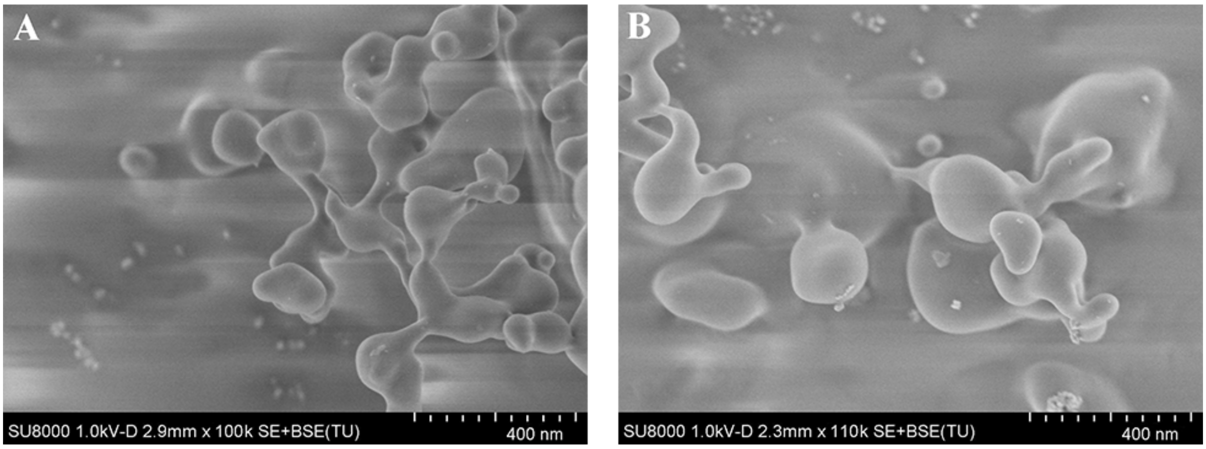

Fig. S3. SEM images of dry dehydroabietic acid and salicylic acid films. (A) DHAA; (B) salicylic acid.

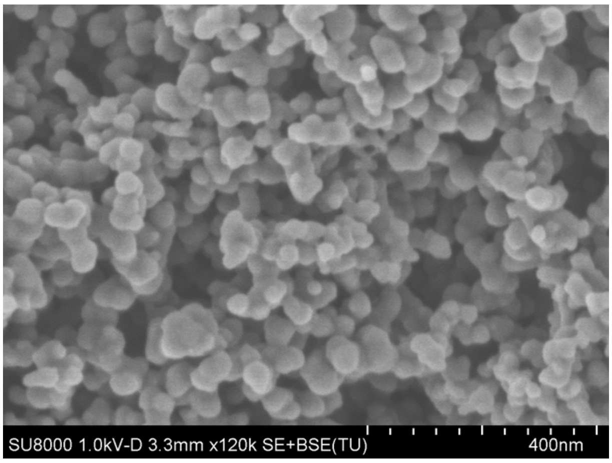

Fig. S4. SEM image of soot particles used in this study.

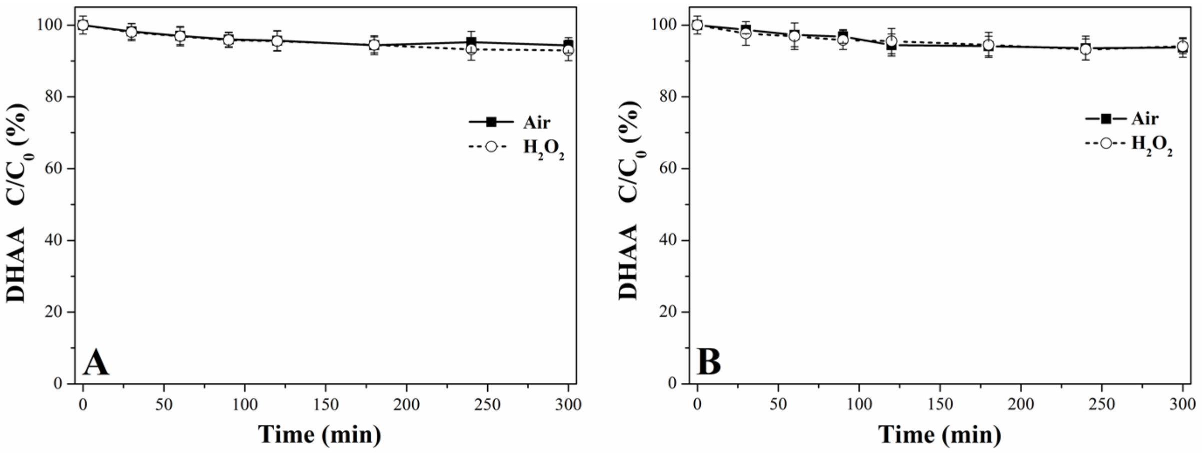

Fig. S5. Vaporization of DHAA in air flow and reaction loss between DHAA and H_2O_2 flow at different temperatures. (n=3, error bars represent 1 standard deviation). (A) Vaporization of DHAA at 5 °C; (B) Vaporization of DHAA at 30 °C.