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用于研究大气氧化过程和机制的双反应器烟雾箱的评估和应用

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Evaluation and Application of Dual-Reactor Chamber for Studying Atmospheric Oxidation Processes and Mechanisms

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Modification of MCM model

In MCM model of C_3H_6 photooxidation, there are many photolysis reactions, and here we just list them as follows:

J_1: O_3=O (^{1}D)+O_2;

J_2: O_3=O+O_2;

J_3: H_2O_2=OH+OH;

J_4: NO_2=NO+O;

J_5: NO_3=NO+O_2;

J_6: NO_3=NO_2+O;

J_7: HONO=OH+NO;

J_8: HNO_3=OH+NO_2;

J_{11}: HCHO=CO+HO_2+HO_2;

J_{12}: HCHO=H_2+CO;

J_{13}: CH_3CHO=CH_3O_2+HO_2+CO;

J_{15}: $HCOCH_2OOH$=HO_2+CO+HCHO+OH;
$HOCH_2CHO$=HO_2+HCHO+HO_2+CO;
$HCOCO_3H$=HO_2+CO+OH;

J_{17}: $CH_3CHOHCHO$=CH_3CHO+HO_2+CO+HO_2;

J_{22}: ACETOL=CH_3CO_3+HCHO+HO_2;

J_{31}: GLYOX=CO+CO+H_2;

J_{32}: GLYOX=HCHO+CO;

J_{33}: GLYOX=CO+CO+HO_2+HO_2;

J_{34}: MGLYOX=CH_3CO_{3+}CO+HO_2;
$HCOCO_2H$=HO_2+HO_2+CO;

J_{41}: $PR1O_2HNO_3$=$PRONO_3AO$+OH;
$PR2O_2HNO_3$=$PRONO_3BO$+OH;
$HYPROPO_2H$=HYPROPO+OH;
$IPROPOLO_2H$=IPROPOLO+OH;
CH_3OOH=CH_3O+OH;
CH_3CO_3H=CH_3O_2+OH;
$HCOCH_2OOH$=$HCOCH_2O$+OH;
$PRNO_3CO_3H$=CH_3CHO+NO_2+OH;
IPROPOLPER=CH_3CHO+HO_2+OH;
$HCOCO_3H$=HO_2+CO+OH;
$HOCH_2CO_3H$=HCHO+HO_2+OH;

J_{51}: CH_3NO_3=CH_3O+NO_2;

J_{56}: $CHOPRNO_3$=PROPALO+NO_2;
NOA=CH_3COCH_2O+NO_2;

J_{57}: $CHOPRNO_3$=HO_2+CO+CH_3CHO+NO_2;
NOA=CH3CO_3+HCHO+NO_2

where J is the photolysis rate of every reaction, more details about the abbreviation of species can be searched on website: http://mcm.leeds.ac.uk/MCM.

In our experiments, all the light sources are in the UV range, so we remove the photolysis reaction at visible wavelengths, which is J_5 and J_6, in our simulation model for all runs of experiments.

For experiments under the irradiation of 365 nm black lights, we also use the modified model. As we know, there are some reactions under the irradiation of 300-350 nm, and these reactions cannot be activated under 365 nm black lights. Considering this situation, we remove J_1 (<315 nm), J_8 (<335 nm), J_{12} (<320 nm), J_{13} (<340 nm), J_{15} (<350 nm), J_{17} (<340 nm), J_{22} (<330 nm) and J_{51} (<310 nm) in the modified model for black lights experiments.

Photooxidation mechanism of VOCs

Fig.S1 illustrates the simplified mechanism of photooxidation of VOCs to form SOA (A) or ozone (B). VOCs react with OH and form RO_2, and RO_2 has three reaction pathways: RO_2, NO and HO_2. The reaction rate of RO_2+RO_2 is very slow and this pathway accounts for less than 1% of total RO_2 reacted. RO_2 mainly reacts with HO_2 and NO to form condensable products. Condensable products may stay in the gas phase or lose or further photolysis, uniformly called path "X" in Fig.S1, and may also condense to form SOA. Specifically, for *m*-xylene, it reacts with OH to form aromatic-OH adduct, and aromatic-OH adduct react with O_2 to form RO_2 or react with NO_2 to form nitrogen-containing ring-retaining products. Aromatic-OH adduct could also form phenol-type products.

B1 and B2 in Fig.S1 show the formation process of ozone. In the absence of VOCs, NO, NO_2 and O_3 concentrations keep balance under irradiation (B2); in the presence of VOCs, NO reacts with RO_2 and form RO and NO_2 (B1), which broke the balance and ozone is accumulated.

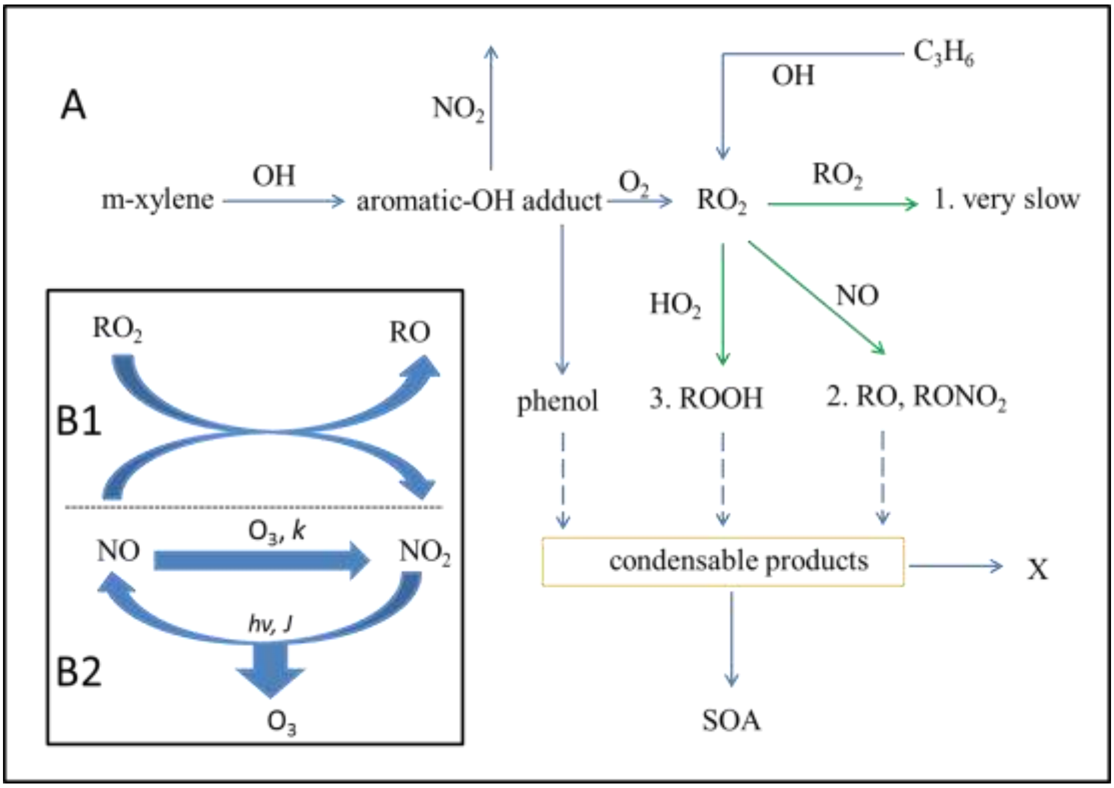

Fig.S1 Schematic diagram of SOA and ozone formation mechanism

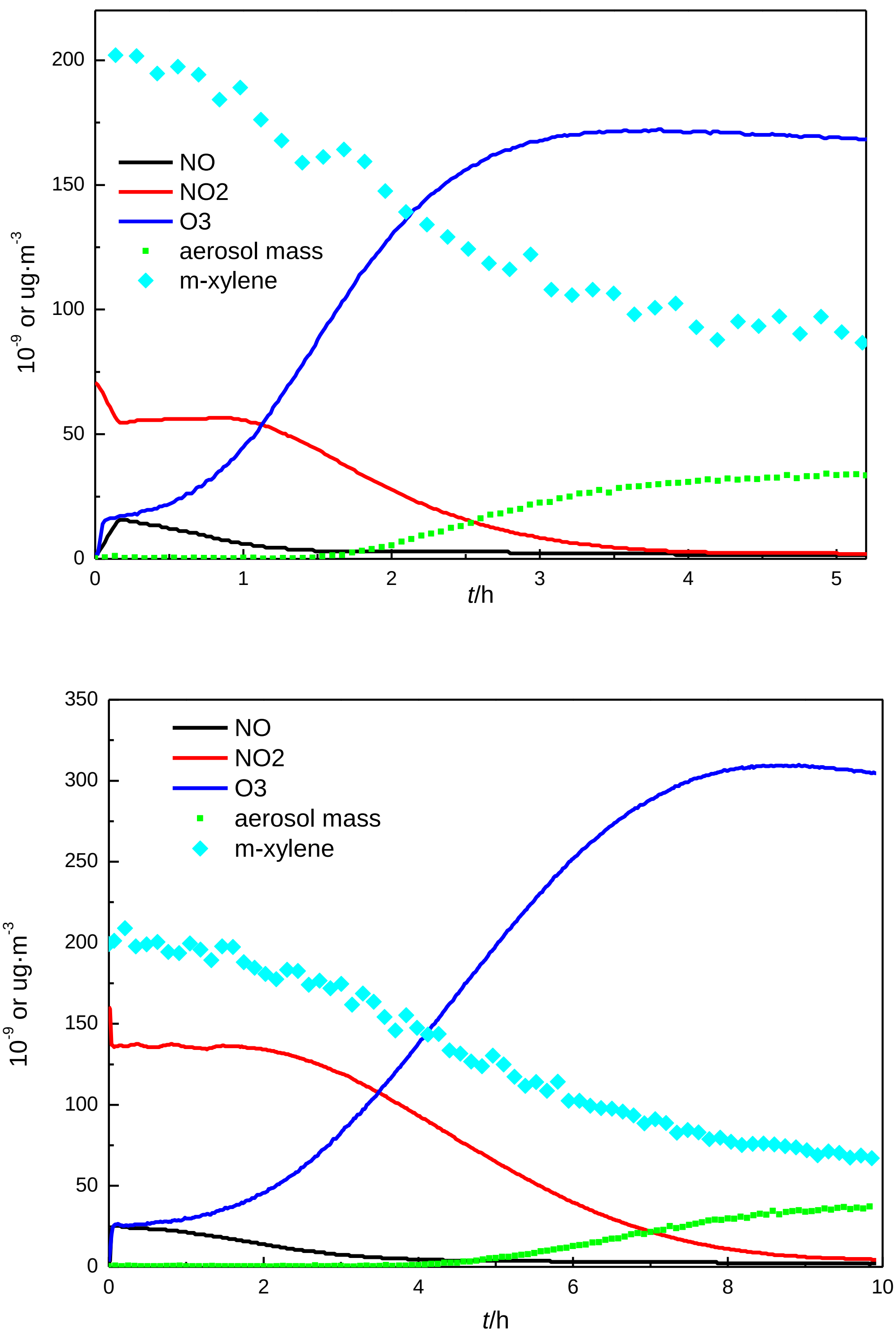

Fig.S2 Reaction profiles of *m*-xylene and NO_x under high HC/NO_x condition (top) and low HC/NO_x condition (bottom)

The unit of aerosol mass is μg·m^{-3}, and the units of other species are 10^{-9}.