

1 **Supporting Information**

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5 **Heterogeneous Reactions of Pirimiphos-methyl and Pirimicarb with NO<sub>3</sub>**

6 **Radicals**

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## 22 1. Calculation of the initial gas/particle distribution ratios

23 The initial gas/particle distribution ratios are calculated according to the vapor  
24 pressure and initial mass concentrations of the particle-bound pesticide measured by  
25 SMPS. Take PMM for example, the initial mass of gas-phase PMM ( $m$ ) is calculated  
26 by the Eq. 1.

$$27 \frac{P_1}{P} = \frac{V_1}{V} = \frac{\frac{m}{M} \times 24.0}{V} \quad (1)$$

28 Where:  $P_1$  is the partial pressure of gas-phase PMM,  $2.0 \times 10^{-3}$  Pa (20 °C);

29  $P$  is atmospheric pressure, 101325 Pa;

30  $V_1$  is partial volume of gas-phase PMM in the chamber;

31  $V$  is the total volume of chamber, 180 L;

32  $M$  is the molar mass of PMM, 305 g/L;

33 The molar volume of gas at 20 °C is 24.0 L/mol.

34 The initial mass concentration of the particle-bound PMM is  $471 \mu\text{g m}^{-3}$ . The mass  
35 of the particle-phase PMM are calculated using the following Eq. 2.

$$36 471 \mu\text{g} / \text{m}^3 \times 180 \text{ L} = 84.8 \mu\text{g} \quad (2)$$

37 Thus, the initial gas/particle distribution ratios are calculated to be  $\sim 1/2$ .

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## 39 2. Calculation of the atmospheric lifetime

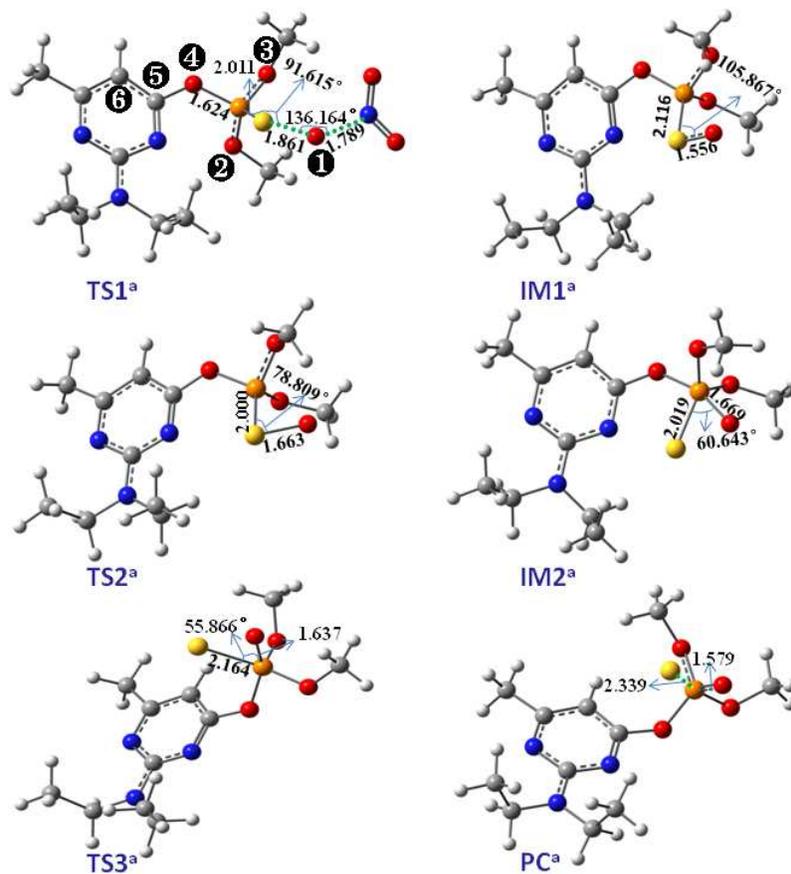
40 The following equation is used to estimate the atmospheric lifetimes of the two  
41 pesticides.

$$42 \tau = \frac{(R_p^3 - R_c^3) \rho_{pes} N_A \eta_{pes}}{3M_{pes} R_p D_g C_{NO_3} \gamma} \quad (3)$$

43 Where  $C_{NO_3}$  is the typical tropospheric concentration of  $NO_3$  radicals at night ( $5 \times 10^8$   
 44 molecules  $cm^{-3}$ ).  $D_g$  is the diffusion coefficient of  $NO_3$  radicals in air ( $\sim 0.12 \text{ cm}^2$   
 45  $s^{-1}$ )(Rudich et al. *Chem. Phys. Lett.* 1996, 261(4-5), 467-473). Thus, the atmospheric  
 46 lifetimes of the PMM and PM particles exposed to  $NO_3$  radicals at night are  
 47 calculated to be  $\sim 6$  and 21 days, respectively.

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49 **3. Geometrial structures of the optimized stationary points for the reaction**  
 50 **pathway of Product I<sup>a</sup>.**



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52 Figure S1. The B3LYP/6-31G(d) optimized stationary points for the reaction pathway  
 53 of Product I<sup>a</sup>. Parameters noted for dashed lines correspond to fixed distances.