

## Supporting info

### Gas-phase Oxidation of NO<sub>2</sub> to HNO<sub>3</sub> by Phenol: Atmospheric Implications

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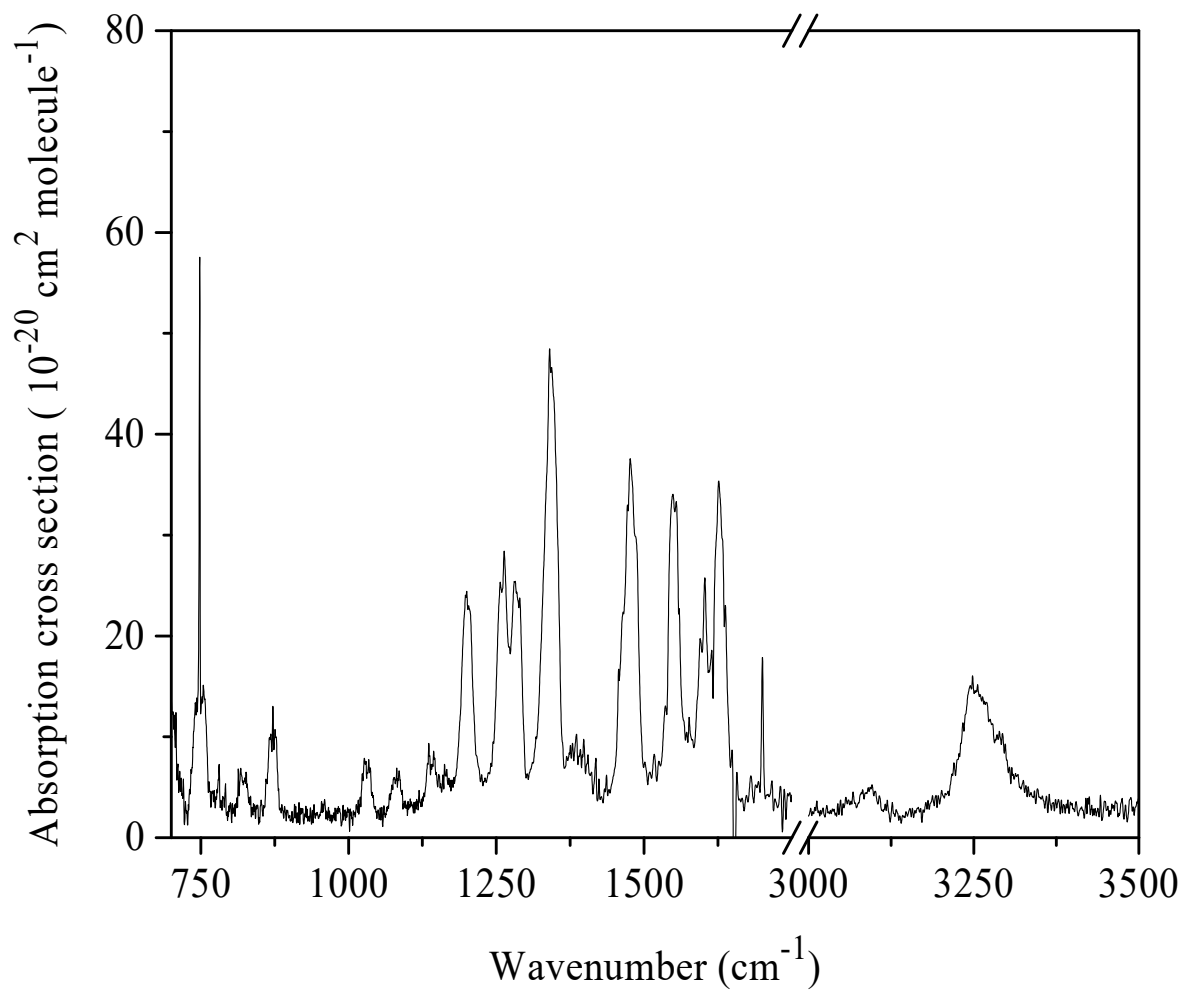
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Supporting information includes 2 Figures, 1 Table, and 6 pages.

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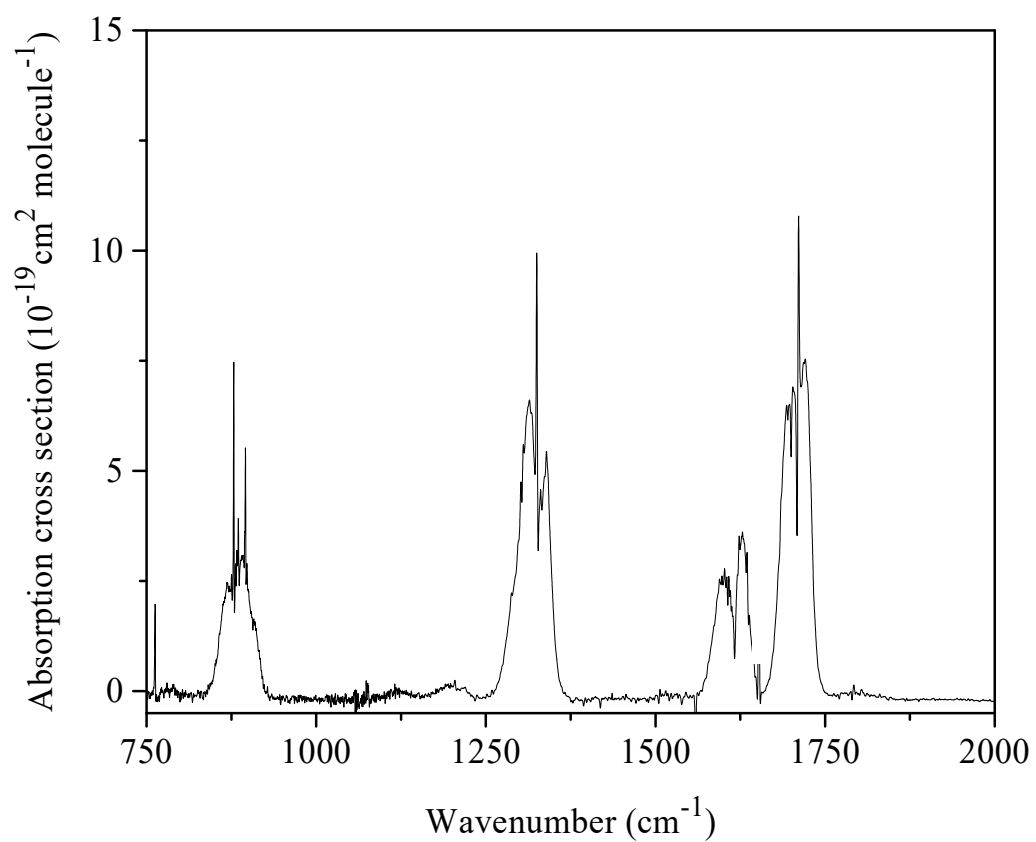
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S 1a: FTIR spectrum of *o*-nitrophenol



Spectrum of  $\text{HNO}_3$  was recorded after diluting 2 mbar of  $\text{HNO}_3$  to 1 bar by using UHP  $\text{N}_2$ .

S 1b: FTIR Spectrum of nitric acid



Spectrum of *o*-nitrophenol was recorded after diluting 400 mbar of *o*-nitrophenol- $\text{N}_2$  mixture to 1 bar by using UHP  $\text{N}_2$ .

S 2a: Calculation of second order rate law:

Rate law for the reaction



Rate of the reaction:

$$-d[A]/dt = k[A][B] \quad \text{-----1}$$

Integrated form of this differential equation is

$$\ln([A]_0[B])/([A][B]_0) = k([A]_0 - [B]_0)t \quad \text{-----2}$$

Where  $[A]_0$  = initial concentration of A and  $[A]$  = concentration of A at t time

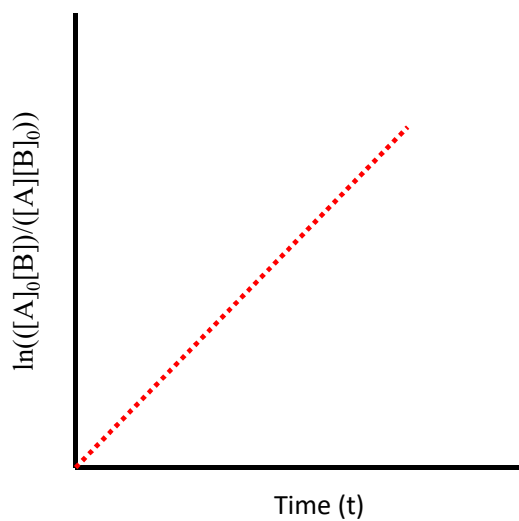
$[B]_0$  = initial concentration of B and  $[B]$  = concentration of B at t time

So the plot of  $\ln([A]_0[B])/([A][B]_0)$  vs t will be a straight line and slope of the plot =  $k([A]_0 - [B]_0)$

In our case

A = PhOH

B = N<sub>2</sub>O<sub>4</sub>



S 2b: Calculation of third order rate law:

Rate law for the reaction



Rate of the reaction:

$$-d[A]/dt = k[A]^2[B] \quad \text{-----1}$$

Integrated form of this differential equation is

$$\ln \left( \frac{([B]_0 [A])}{([A]_0 [B])} \right) + \frac{2([B]_0 - [B])(2[B]_0 - [A]_0)}{([A]_0 [A])} = kt(2[B]_0 - [A]_0)^2 \quad \text{---2}$$

Where  $[A]_0$  = initial concentration of A and  $[A]$  = concentration of A at t time

$[B]_0$  = initial concentration of B and  $[B]$  = concentration of B at t time

So the plot of  $\ln \left( \frac{([B]_0 [A])}{([A]_0 [B])} \right) + \frac{2([B]_0 - [B])(2[B]_0 - [A]_0)}{([A]_0 [A])}$  vs t will be a straight line and slope of the plot =  $kt(2[B]_0 - [A]_0)^2$

If  $Y = \ln \left( \frac{([B]_0 [A])}{([A]_0 [B])} \right) + \frac{2([B]_0 - [B])(2[B]_0 - [A]_0)}{([A]_0 [A])}$  taken then plot of Y vs t will be a straight line passing through origin.

In our case

A = NO<sub>2</sub>

B = PhOH

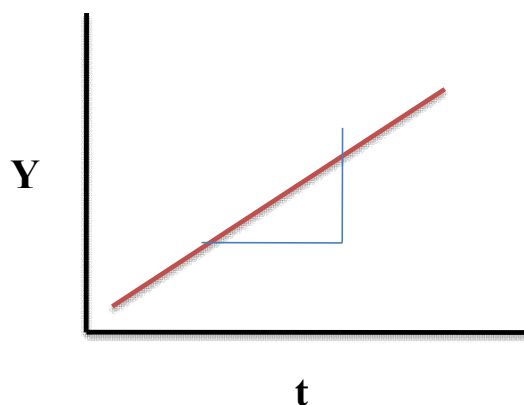


Table S 1

Frequencies (cm <sup>-1</sup> )	Species	Vibrational mode	Absorption cross-section (cm <sup>2</sup> molecule <sup>-1</sup> )
878	HNO <sub>3</sub>	-NO <sub>2</sub> deformation	6.81×10 <sup>-19</sup>
1325	HNO <sub>3</sub>	-NO symmetric stretching	9.95×10 <sup>-19</sup>
1711	HNO <sub>3</sub>	-NO anti symmetric stretching	1.04×10 <sup>-18</sup>
748	<i>o</i> -nitrophenol	-OH bending	5.70×10 <sup>-19</sup> <sup>a</sup>
3250	<i>o</i> -nitrophenol	-OH stretching	1.61×10 <sup>-19</sup> <sup>a</sup>
1875	NO	NO stretching	1.03×10 <sup>-19</sup>

a = estimated in the present study.

**Table S 1:** Characteristic vibrational frequencies of the species identified, and absorption cross-sections of the particular modes according to PNNL<sup>48</sup> database. Absorption cross-section of *o*-nitrophenol has been estimated in the present study (a).