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#### Absorption Cross Sections of 2-Nitrophenol in the 295-400 nm Region, and Photolysis of 2-Nitrophenol at 308 and 351 nm Manuvesh Sangwan and Lei Zhu\* Wadsworth Center, New York State Department of Health, and Department of Environmental Health Sciences, University at Albany Albany, NY 12201-0509 \*Corresponding author. Tel: 518-474-6846; fax: 518-473-2895; e-mail: zhul@wadsworth.org.

### Abstract

2-Nitrophenol is an important component of "brown carbon" in the atmosphere. Photolysis is its dominant gas phase removal process. We have determined the gas phase absorption cross sections of 2-nitrophenol in the 295-400 nm region by using cavity ring-down spectroscopy. 2-Nitrophenol exhibits broad absorption band over the wavelength region studied. with peak absorption located at 345 nm. Absorption cross section values range between  $(2.86\pm0.18)\times10^{-18}$  and  $(2.63\pm0.31)\times10^{-20}$  cm<sup>2</sup>/molecule over the 295-400 nm range. We have investigated the HONO, NO<sub>2</sub>, and OH formation channels following the gas phase photolysis of 2-nitrophenol at 308 and 351 nm. Direct NO<sub>2</sub> formation was not observed. HONO and OH are direct products from 2-nitrophenol photolysis. The average OH quantum yields from the photolysis of 0.5, 1.0, and 2.0 mTorr of 2-nitrophenol are 0.69±0.07 and 0.70±0.07 at 308 and 351 nm. The average HONO quantum yields are 0.34±0.09 and 0.39±0.07 at 308 and 351 nm. The OH and HONO quantum yields are independent of nitrogen carrier gas pressure in the 20-600 Torr range. Oxidant formation rate constants from 2-nitrophenol photolysis have been calculated. Discussions have been made concerning the role of 2-nitrophenol gas phase photolysis in the formation of atmospheric oxidants in regions of high anthropogenic emissions.

#### 1. Introduction

The significantly elevated daytime nitrous acid (HONO) concentrations<sup>1-5</sup> compared to those predicted based on the photo stationary state between HONO sources and sinks lead to the postulate that HONO is produced by photochemical sources. One proposed HONO source is gas phase photolysis<sup>6</sup> of 2-nitrophenol (o-C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)OH) over the 300-500 nm region. 2-Nitrophenol is emitted from the burning of coal and wood and from industrial sources such as manufacturers of phenol-formaldehyde resins, dyes, explosives, and pharmaceutical drugs.<sup>7</sup> It can be formed from OH radical-initiated oxidation of phenol in the presence of NO<sub>x</sub> or reaction of phenol with nitrate radicals.<sup>8-10</sup> 2-Nitrophenol has been observed in the gas, particle, and condensed phases of the environment.<sup>7,11-16</sup> It is phytotoxic.<sup>17</sup> Reported gas phase concentrations<sup>18-23</sup> of 2-nitrophenol vary with geographic locations; they are in the range of 0.8-350 ng/m<sup>3</sup> (i.e., 0.14 to 62 pptv).

2-Nitrophenol in aqueous solution absorbs strongly in the near UV region.<sup>24</sup> There have been one reported study<sup>25</sup> of the gas phase near UV absorption spectrum of 2-nitrophenol in the 320-450 nm region using incoherent broad-band cavity enhanced absorption spectroscopy. But the absorption cross section data are only qualitative in nature. Also, absorption cross section values have not been obtained in the 290-320 nm region. Moreover, it is unclear why the reported gas phase 2-nitrophenol cross section values are 11-91 times larger than the gas phase absorption cross sections of 2-nitrobenzaldehyde,<sup>26</sup> another nitro-aromatic compounds. Given the key role 2-nitrophenol gas phase photolysis likely plays in atmospheric HONO formation, there is clearly a need to quantitatively determine the near UV absorption cross section values of this compound so that contribution of gas phase 2-nitrophenol photolysis to HONO formation can be quantified. The ortho position of the OH and NO<sub>2</sub> groups in 2-nitrophenol enables strong intramolecular hydrogen bonding interaction to form aci-nitro isomer;<sup>27,28</sup> the structure and confirmation of which were identified<sup>29</sup> by a combination of matrix isolation infrared spectroscopy and density-functional theory calculations. The aci-nitro isomer of 2-nitrophenol was postulated<sup>6</sup> as an intermediate in HONO formation in the near UV photolysis of 2-nitrophenol in the liquid<sup>30</sup> and gas phase<sup>6</sup>. But the HONO quantum yield from the gas phase photodissociation of 2-nitrophenol and the variation of the HONO quantum yield with excitation wavelength have not been reported. Formation of OH radical was observed by laser induced fluorescence from gas phase photodissociation dynamics studies<sup>31,32</sup> of 2-nitrophenol at 266 nm, 355 nm, and in the 361-390 nm range. However, the corresponding OH quantum yields were not measured. As a result of lacking quantitative product quantum yield information, it has not been possible to assess the extent of oxidant formation from 2-nitrophenol photolysis in the atmosphere.

In this paper, we present results obtained from quantitative measurements of the gas phase absorption cross sections of 2-nitrophenol over the 295-400 nm range, by using cavity ring-down spectroscopy<sup>33,34</sup>. We have investigated the HONO, NO<sub>2</sub>, and OH formation channels following the 308 and 351 nm photolysis of 2-nitrophenol. The OH and the HONO quantum yields have been obtained. We have estimated the atmospheric oxidant formation rate constants following the gas phase photolysis of 2-nitrophenol using 2-nitrophenol near UV absorption cross sections, and OH and HONO formation quantum yields obtained from the current study.

#### 2. Experimental technique

Gas-phase absorption cross sections of 2-nitrophenol in the 295-400 nm region were measured in a 48 cm long ring-down cavity. Both ends of the cavity cell were vacuum-sealed by a pair of high reflectance cavity mirrors. High-reflectance cavity mirrors with centering Page 5 of 35

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wavelengths at about 307 nm, 325 nm, 355 nm, and 373 nm were used; the corresponding wavelength intervals for high reflectivity are 295-320 nm, 310-341 nm, 331-378 nm, and 339-407 nm. Detailed descriptions of our experimental setup can be found elsewhere.<sup>35-38</sup> The probe beam over the 295–400 nm range was generated by frequency doubling the output of a dye laser (Continuum, ND6000) pumped by the second harmonic of a Nd:YAG laser (Continuum, Surelite II). The probe beam entered the ring-down cavity through the front cavity mirror. Dye solutions of Rhodamin 610, Rhodamin 640, 4-dicyanmethylene-2-methyl-6-(p-dimethylamino styryl)-4H-pyran (DCM), pyridine 1 (LDS-698), LDS751, LDS 765 and LDS 821 were used. Photon intensity decay inside the cavity was monitored by a photomultiplier tube (PMT) placed behind the rear cavity mirror. The output of PMT was amplified, digitized, and sent to a computer. The decay profile was fitted with a single-exponential decay function to calculate the ring-down time constant ( $\tau$ ) and the total loss ( $\Gamma$ ) per round-trip pass. The absorbance of 2nitrophenol was obtained by measuring cavity losses in the presence and absence of 2nitrophenol. The optical path length is 48 cm. The gas pressure inside the cell was monitored by MKS Baratron capacitance manometers (0.1 and 1 Torr full scale; most of the measurements were made using 0.1 Torr full-scale pressure gauge). Before every experiment, the cavity cell was pumped to  $10^{-5}$  Torr. For absorption cross section measurements, pure 2-nitrophenol was used; the pressure range used varied between  $5.0 \times 10^{-4}$  and  $1.5 \times 10^{-2}$  Torr. The highest 2nitrophenol pressure used  $(1.5 \times 10^{-2} \text{ Torr})$  was constrained by the strong near UV absorption of 2nitrophenol. Pressure measurement uncertainty is estimated in the range of 2.5%-0.5% for the 2nitrophenol pressure of  $5.0 \times 10^{-4}$  to  $1.5 \times 10^{-2}$  Torr when a 0.1 Torr full-scale Baratron capacitance monometer was used. The cell was evacuated to the initial vacuum conditions before a fresh sample of 2-nitrophenol was added. Cross section measurements were made under static conditions.

Photolysis of 2-nitrophenol was carried out by combining excimer laser photolysis at 308 nm and at 351 nm with cavity ring-down spectroscopy. The output from an excimer laser (Coherent COMPEX Pro102) was directed into the stainless steel reaction cell at a 15<sup>°</sup> angle with the main cell axis through a side arm. With a 12mm wide and 6 mm tall apertured photolysis beam, the illumination volume of the photolysis beam through the level arm is about 27.4 cm<sup>3</sup>. The probe beam entered the cell along the main cell axis. At the center of the cavity, the pump beam and the probe beam overlapped geometrically. The overlap region of the photolysis and the probe laser is a rectangular solid with its center overlapping that of the cell, and its width and height defined by the dimension of the apertured photolysis beam; the length of the rectangular solid is defined by (beam width)  $\times$  (tan15°)<sup>-1</sup>, where 15° is the crossing angle between the pump and the probe laser beams. The length of the photolysis/probe laser overlap region is defined by (beam width)  $\times$  (sin15°)<sup>-1</sup>. The length of the photolysis/probe laser overlap region is about 4.6 cm with a 12 mm wide photolysis beam. The delay time between the firing of the photolysis laser and the firing of the probe laser was varied with a pulse/delay generator. Formation of HONO and possible NO<sub>2</sub> products from the 2-nitrophenol photolysis was monitored by their near UV absorptions<sup>39-46</sup> in the 364 - 370 nm region. Production of OH from the photolysis of 2-nitrophenol was detected by OH radical's characteristic sharp absorption band<sup>47</sup> in the 307.80-308.30 nm region. Absolute OH absorption was calibrated relative to that from the 308 nm photolysis of nitric acid. Product absorptions from the photolysis of 2nitrophenol were obtained by measurement of the cavity losses in the presence of 2-nitrophenol, with and without photolysis. The photolysis beam energies prior to its entrance into the cell and

after its exit from an empty cell were measured by a calibrated joulemeter. The incident beam energy inside the cell was corrected for transmission loss of the photolysis beam at the front cell window, and for reflection of the photolysis beam from the rear cell window.

#### Reagents and Bath Gas Used and Synthetic Processes of HNO<sub>3</sub> and HONO

2-Nitrophenol was obtained as a yellow crystalline powder from Sigma-Aldrich with  $\geq$ 98% purity. It was stored in a glass bulb connected to the cavity cell and was pumped for about Before running the experiments, the 2-nitrophenol pressure of about 0.1 Torr was 1 hr. introduced into the cell; the sample was kept in the cavity cell for about 45 min before it was completely evacuated. This procedure of conditioning the cell wall minimized the loss of gas phase 2-nitrophenol sample during cross section and photolysis product measurements. Nitrogen carrier gas (Airgas; ≥99.999% purity) was used without further purification. Nitric acid was prepared<sup>48</sup> by vacuum distillation of a 3:2 mixture of sulfuric acid (98%; Mallinckrodt Baker) and nitric acid (70%; Mallinckrodt Baker) at 273 K; the distilled HNO<sub>3</sub> was collected into a trap cooled to ethanol/dry ice temperature (195 K). At least four successive distillations were conducted to purify the HNO<sub>3</sub> sample. To further reduce NO<sub>2</sub> impurity in HNO<sub>3</sub>, an extra distillation of the HNO<sub>3</sub> sample was done on the day of the experiment. HONO was prepared by mixing 1:1:2 mixture of NO<sub>2</sub>:NO:H<sub>2</sub>O in a gas bulb and allowing for at least 24 hours for the reaction  $NO_2+NO+H_2O = 2HONO$  to reach equilibrium.  $NO_2$  was obtained from Sigma-Aldrich ( $\geq$ 99.5% purity) and NO was obtained from Airgas ( $\geq$ 99.5% purity). Liquid H<sub>2</sub>O from a Barnstead nanopure ultrapure water system (Thermo Scientific, USA) was freeze-pump-thawed for three times before water vapor was used in HONO synthesis. All experiments were conducted at an ambient temperature of 295±2 K.

3. Results and discussion

#### 3.1. Gas phase absorption cross sections of 2-nitrophenol in the 295-400 nm region.

We have obtained gas phase absorption cross sections of 2-nitrophenol at 5 nm intervals in the 295-400 nm region by using cavity ring-down spectroscopy. Absorption cross section at each wavelength was obtained by measurement of the round-trip absorbance by 2-nitrophenol as a function of the 2-nitrophenol pressure in the cavity. Round-trip absorbance at a given 2nitrophenol pressure was determined from the differential measurement of cavity losses in the absence and in the presence of 2-nitrophenol. Shown in Figure 1 is round-trip absorbance plotted against 2-nitrophenol pressure at 300 nm, 330 nm, 355 nm, and 385 nm, respectively.



Figure 1. Round-trip absorbance as a function of the 2-nitrophenol pressure at 300 nm, 330 nm, 355 nm, and 385 nm. The solid lines are linear regression analysis of experimental data from which absorption cross sections of  $1.39 \times 10^{-18}$ ,  $1.74 \times 10^{-18}$ ,  $1.03 \times 10^{-18}$ , and  $2.98 \times 10^{-19}$  cm<sup>2</sup>/molecule were extracted at 300 nm, 330 nm, 355 nm, and 385 nm, respectively.

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From the slope of the linear regression analysis, 2-nitrophenol absorption cross sections of  $(1.39\pm0.08)\times10^{-18}$ ,  $(1.74\pm0.11)\times10^{-18}$ ,  $(1.03\pm0.04)\times10^{-18}$ , and  $(2.98\pm0.08)\times10^{-19}$  cm<sup>2</sup>/molecule were extracted at 300 nm, 330 nm, 355 nm, and 385 nm. Listed in Table 1 and plotted in Figure 2 are absorption cross sections of 2-nitrophenol as a function of wavelength. 2-Nitrophenol exhibits broad spectral absorption in the 295-400 nm region, with peak absorption located at 345 nm. The near UV absorption spectrum of 2-nitrophenol<sup>49</sup> originates from the  $\pi \rightarrow \pi^*$  transition between the benzene ring and the nitro group. Absorption cross section values vary between  $(2.86\pm0.18)\times10^{-18}$  and  $(2.63\pm0.31)\times10^{-20}$  cm<sup>2</sup>/molecule over the wavelength range studied. Errors quoted  $(1\sigma)$  are relative errors derived from standard deviation of about 3 **Table 1. Gas phase absorption cross sections (\sigma, in unit of cm<sup>2</sup>/molecule, base e) of 2-nitrophenol as** 

a function of wavelength ( $\lambda$ ).

$\lambda$ (nm)	$\sigma$ (this work) <sup>a</sup>	$\sigma$ (Chen <i>et al.</i> )
295	$(1.47\pm0.11)\times10^{-18}$	
300	$(1.36\pm0.08)\times10^{-18}$	
305	$(1.10\pm0.12)\times10^{-18}$	
310	$(1.44\pm0.10)\times10^{-18}$	
315	$(1.77\pm0.19)\times10^{-18}$	
320	$(1.80\pm0.15)\times10^{-18}$	9.26×10 <sup>-18</sup>
325	$(1.60\pm0.18)\times10^{-18}$	$1.52 \times 10^{-17}$
330	$(1.98\pm0.17)\times10^{-18}$	$1.60 \times 10^{-17}$
335	$(2.03\pm0.19)\times10^{-18}$	$1.66 \times 10^{-17}$
340	$(2.23\pm0.12)\times10^{-18}$	$1.66 \times 10^{-17}$
345	$(2.86\pm0.18)\times10^{-18}$	$1.48 \times 10^{-17}$
350	$(2.29\pm0.21)\times10^{-18}$	$1.33 \times 10^{-17}$
355	$(1.12\pm0.05)\times10^{-18}$	$1.18 \times 10^{-17}$
360	$(9.37\pm0.29)\times10^{-19}$	$8.83 \times 10^{-18}$
365	(8.16±0.38)×10 <sup>-19</sup>	6.35×10 <sup>-18</sup>
370	$(7.24\pm0.25)\times10^{-19}$	4.65×10 <sup>-18</sup>
375	$(6.26\pm0.29)\times10^{-19}$	$3.40 \times 10^{-18}$
380	$(3.73\pm0.16)\times10^{-19}$	$2.03 \times 10^{-18}$
385	$(2.88\pm0.12)\times10^{-19}$	$1.13 \times 10^{-18}$
390	$(9.29\pm0.38)\times10^{-20}$	6.30×10 <sup>-19</sup>
395	$(3.10\pm0.10)\times10^{-20}$	3.40×10 <sup>-19</sup>
400	$(2.63\pm0.31)\times10^{-20}$	2.00×10 <sup>-19</sup>

<sup>a</sup>Errors quoted are  $1\sigma$  standard deviations in the precision of the measurements.

independent cross section measurements. Factors contributing to the systematic uncertainties include absolute uncertainties in pressure and absorption measurements and accurate knowledge of the 2-nitrophenol concentration in the cell. An up to 2% impurity was specified for 2-nitrophenol crystalline powder. Despite pumping the 2-nitrophenol powder in a glass vessel for an extended period of time before the experiments and pumping 2-nitrophenol powder before each fill, and quick sample filling time to minimize the effect of outgassing from the chamber wall, the overall uncertainty of gas phase 2-nitrophenol concentration is expected to be more than 2%.



Figure 2. Absorption cross section of 2-nitrophenol as a function of wavelength over the 295-400 nm range. Circles represent cross section data obtained in the present work. The solid line denotes cross section data reported in Reference 25.

Shown in Figure 2 for comparison are previously reported<sup>25</sup> gas phase absorption cross sections of 2-nitrophenol in the 320-400 nm region. Both the spectral shape and the absolute cross section values differ between the literature study and the current study. Literature absorption cross sections of 2-nitrophenol<sup>25</sup> vary from  $9.26 \times 10^{-18}$  cm<sup>2</sup>/molecule at 320 nm to  $1.66 \times 10^{-17}$  cm<sup>2</sup>/molecule at 335 nm, and to  $2.00 \times 10^{-19}$  cm<sup>2</sup>/molecule at 400 nm. Absorption

cross sections of 2-nitrophenol obtained in this study range from  $(1.80\pm0.15)\times10^{-18}$  cm<sup>2</sup>/molecule at 320 nm to  $(2.03\pm0.19)\times10^{-18}$  cm<sup>2</sup>/molecule at 335 nm, and to  $(2.63\pm0.31)\times10^{-20}$  at 400 nm. Thus, literature absorption cross sections of 2-nitrophenol are 5.1 times, 8.2 times, and 7.6 times our cross section values at 320 nm, 335 nm, and 400 nm. Such large cross section differences likely result from the lack of validation of an experimental method for low vapor pressure species and lack of choosing proper experimental conditions in this literature study. Although the literature study<sup>25</sup> reported similar cross section values for benzaldehyde using incoherent broad-band cavity enhanced absorption spectroscopy compared with those obtained previously by our group<sup>26</sup> using cavity ring-down spectroscopy, the room temperature vapor pressure of 2nitrophenol ( $\sim 0.1$  Torr) is about one order of magnitude lower than that of benzaldehyde. Both cavity ring-down spectroscopy and cavity enhanced absorption spectroscopy are not backgroundfree absorption detection method. In order to obtain quantitative absorption values, it is important that the measured absorption is distinguishable from the measured background cavity loss. One set of cavity mirrors were used in the cavity enhanced spectroscopic measurement of 2-nitrophenol absorption, with a reflectivity of up to 99% for both mirrors at the wavelengths of highest reflectivity. We used several sets of mirrors; the mirror reflectivity at a wavelength region of high reflectivity (99.8%-99.9%) is about one order of magnitude higher than that of the literature study. The maximum mixing ratio of 90 ppbv of 2-nitrophenol was used in the literature study<sup>25</sup>, which would translate to the maximum 2-nitrophenol partial pressure of  $6.8 \times 10^{-5}$  Torr. The minimum 2-nitrophenol pressure we used was  $5.0 \times 10^{-4}$  Torr. The minimum 2-nitrophenol pressure we used in the cross section determination is 7.3 times the maximum pressure used in the prior study. The literature study did not provide Beer's law absorption calibration over a range of 2-nitrophenol pressure at any representative wavelength. We

obtained cross section values from Beer's law plot at each wavelength. The combination of high mirror loss, low 2-nitrophenol pressure used, and small absorption value relative to the large background mirror loss let us conclude this literature study is qualitative in nature.

Gas-phase absorption cross sections of 2-nitrophenol in the 295-400 nm region determined in the current study are compared to those<sup>26</sup> of 2-nitrobenzaldehyde, the only other multi-functional aromatic compound with nitro substitution, whose gas phase absorption cross section data are available. Cross section values for both compounds are plotted in Figure 3. Absorption cross sections of 2-nitrophenol are larger than those of 2-nitrobenzaldehyde over the wavelength region studied. Since the origin of the near UV absorption band for 2-nitrophenol<sup>49</sup> is that of the  $\pi \rightarrow \pi^*$  transition from the NO<sub>2</sub> group whereas the near UV absorption band for 2-nitrobenzaldehyde results from the n $\rightarrow \pi^*$  transitions from the NO<sub>2</sub> and the CHO groups,<sup>50</sup> the larger near UV absorption cross section values for 2-nitrophenol compared to those for 2-



Figure 3. Absorption cross sections of 2-nitrophenol and 2-nitrobenzaldehyde as a function of wavelength over the 295-400 nm range. Circles denote 2-nitrophenol cross section values obtained from the current study. Squares represent 2-nitrobenzaldehyde cross section data obtained by Xiang *et al.*<sup>26</sup>

nitrobenzaldehyde can be rationalized in terms of the larger transition strength of the  $\pi \rightarrow \pi^*$  transition for 2-nitrophenol.

#### 3.2. Photolysis of 2-nitrophenol at 308 and 351 nm.

#### 3.2.1. Time-resolved study of OH radical formation from 2-nitrophenol photolysis.

Formation of OH radical from the photolysis of 2-nitrophenol was investigated by combining excimer laser photolysis at 308 and 351 nm with cavity ring-down spectroscopy. Illustrated in the upper panel of Figure 4 are cavity ring-down spectra plotted against wavelength in the 307.80-308.30 nm region in the absence and presence of 2-nitrophenol photolysis at 308 nm. A sharp absorption band peaking at 308.02 nm appeared immediately after the photolysis. This new absorption band is attributed to that of 2-nitrophenol photodissociation product. The OH radical has well-known  $A^2\Sigma^+$ ,  $v'=0 \leftarrow X^2\Pi$ , v''=0 absorption band<sup>47</sup> around 308 nm. To verify whether the product absorption band at 308.02 nm is that of OH, we measured the OH radical absorption spectrum from the 308 nm photolysis of HNO<sub>3</sub>.<sup>51</sup> Shown in the lower panel of Figure 4 are cavity ring-down spectra with and without 308 nm photolysis of  $HNO_3$ . The spectral feature of the product absorption band formed from 2-nitrophenol photolysis matches that of OH formed from the HNO<sub>3</sub> photolysis. This gives clear indication that the OH radical is formed from 2-nitrophenol photolysis at 308 nm. The OH radical was also observed as a product from the 351 nm photolysis of 2-nitrophenol. By tuning the wavelength of the ring-down probe beam to OH absorption maximum at 308.02 nm and varying the delay time between the firing of the photolvsis laser and the firing of the probe laser, absorption of OH formed from 2nitrophenol photolysis was recorded as a function of time. Figure 5 shows an OH radical roundtrip absorption profile from 308 nm photolysis of 1.0 mTorr of 2-nitrophenol as a function of



Figure 4. Upper panel: cavity ring-down spectra plotted against wavelength in the 307.80-308.30 nm region in the absence and presence of 308 nm photolysis of 2-nitrophenol at 2.0 mTorr pressure. Photolysis/probe laser delay was set at 15 μs.
Wavelength scan was conducted at 0.01 nm interval. Lower panel: cavity ring-down spectra with and without 308 nm photolysis of HNO<sub>3</sub> at 2.0 Torr pressure.

time. OH radical absorption at 308.02 nm increased immediately after the photolysis pulse, and it subsequently decreased rapidly with photolysis/probe laser delay time in the 20-80  $\mu$ s range. The measured initial OH absorption values at 15  $\mu$ s are higher for higher 2-nitrophenol



Figure 5. Transient OH radical round-trip absorption profile from the 308 nm photolysis of 1.0 mTorr of 2-nitrophenol measured at 308.02nm.

pressures. The decay rate of OH radical absorption in the 15-60  $\mu$ s range does not increase with increasing 2-nitrophenol pressure for 2-nitrophenol pressures of 0.5 mTorr, 1.0 mTorr, and 2.0 mTorr. Such results are consistent with literature OH/2-nitrophenol reaction rate constant<sup>52</sup> of  $9.0 \times 10^{-13}$  cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup> and the limited pressure range we varied 2-nitrophenol pressure, which was constrained by strong near UV absorption of the probe beam by the background 2-nitrophenol molecules. The OH decay profiles from the photolysis of 2-nitrophenol at 0.5 mTorr, 1.0 mTorr and 2.0 mTorr pressures were used to extract OH diffusion coefficient in the presence of 2-nitrophenol at mTorr pressure; it is about  $5.9 \times 10^4$  cm<sup>2</sup>/s. Diffusion out of the probe beam likely plays an important role in the decay of OH radical absorption in the 15-80  $\mu$ s range for OH temporal absorption profile shown in Figure 5. Temporal absorption measurement of OH shows that OH radical absorption formed from 2-nitrophenol photolysis in the photolysis/probe laser overlap region decays with photolysis/probe laser delay time, and we need to use OH absorption at 15  $\mu$ s delay time to obtain nascent OH absorption formed from 2-nitrophenol photolysis.

The OH radical quantum yield from the photolysis of 2-nitrophenol was derived from the ratio of the OH concentration produced in the photolysis/probe laser overlap region to the absorbed photon density in the same region. The absorbed photolysis photon density in the photolysis and detection laser overlap region was calculated from the difference between the transmitted photolysis beam energies entering ( $E_{in}$ ) and leaving ( $E_{out}$ ) the overlap region, the individual photolysis photon energy ( $hc/\lambda$ ), and the volume (v) of the overlap region. The photolysis beam energy before and after the photolysis/probe laser overlap region was obtained from the incident photolysis beam energy entering the cell ( $E_0$ ), the absorption cross section ( $\sigma$ ) and the concentration (n) of 2-nitrophenol in the cell, and the absorbing path length, by applying the Beer-Lambert law:

$$E_{\rm in} = E_0 \bullet \exp(-\sigma n l_1) \tag{1}$$

$$E_{\text{out}} = E_0 \bullet \exp(-\sigma n l_2) \tag{2}$$

where  $l_1$  is the distance between the photolysis beam entrance and the beginning of the overlap region, and  $l_2$  is the distance between the photolysis beam entrance and the end of the overlap region. The photon fluence used in the OH quantum yield determination was ~0.04 J/cm<sup>2</sup> at 308 nm and ~0.006 J/cm<sup>2</sup> at 351 nm. Absorbed photolysis photon densities in the pump/probe laser overlap region from the 308 nm photolysis of 0.5, 1.0, and 2.0 mTorr of 2-nitrophenol were estimated to be  $1.4 \times 10^{12}$ ,  $2.8 \times 10^{12}$ , and  $5.5 \times 10^{12}$  molecules/cm<sup>3</sup>, respectively. Absorbed photolysis photon densities from 351 nm photolysis of 2-nitrophenol at 0.5, 1.0, and 2.0 mTorr pressure were  $3.2 \times 10^{11}$ ,  $6.4 \times 10^{11}$ , and  $1.3 \times 10^{12}$  molecules/cm<sup>3</sup>. The OH radical concentration after the 308 or 351 nm photolysis of a 2-nitrophenol sample was obtained by measurement of OH absorption at 308.02 nm at a photolysis and a probe laser delay of 15 µs. Calibration of the absolute OH concentration from the 2-nitrophenol photolysis was made by measurement of OH

absorption from the 308 nm HNO<sub>3</sub> photolysis for which OH formation quantum yield of unity was reported.<sup>51</sup> Absorbed photon densities following the 308 nm photolysis of 0.5 Torr, 1.0 Torr, and 2.0 Torr HNO<sub>3</sub> and the round-trip OH absorptions at 308.02 nm after the photolysis of HNO<sub>3</sub> were determined. Combining experimentally obtained round trip OH absorption for a given HNO<sub>3</sub> pressure with literature OH quantum yield of 1 from the 308 nm photolysis of HNO<sub>3</sub> and the estimated absorbed photolysis photon density by HNO<sub>3</sub> allows us to obtain absolute OH absorption calibration at 308.02 nm. The average OH quantum yields from photodissociation of 2-nitrophenol at 0.5, 1.0, and 2.0 mTorr pressures are 0.69±0.07 at 308 nm and  $0.70\pm0.07$  at 351 nm, where errors quoted (1 $\sigma$ ) represent experimental scatter. Systematic errors in the OH quantum vield measurements include absolute uncertainties in the determination of: OH radical absorption cross section (~13%), 2-nitrophenol concentration (~4%) and absorption cross section (~9% at 308 nm and 351 nm), and photolysis pulse energy (~5% at 308 nm and  $\sim 10\%$  at 351 nm). Considering both random and systematic errors, the overall uncertainties in the determination of the OH quantum yields from 2-nitrophenol photolysis are about 41% at 308 nm, and about 46% at 351 nm. The OH quantum yields are very similar from the 308 nm and 351 nm photolysis of 2-nitrophenol, suggesting that the photon energies at these wavelengths are much higher than the dissociation threshold for 2-nitrophenol to form  $OH+\bullet C_6H_4NO_2$ .

The dependence of the OH quantum yields from the 308 nm and 351 nm photolysis of 2nitrophenol on nitrogen carrier gas pressure was examined. The OH quantum yields at these photolysis wavelengths were found to be independent of the nitrogen carrier gas pressure within experimental error limit in the 20-600 Torr range. Since 2-nitrophenol has a large number of vibrational degrees of freedoms (3N-6 = 39), its intramolecular vibrational and rotational relaxation is much faster than intermolecular collisional quenching by nitrogen. If intramolecular vibrational and rotational relaxation occurs following 308 and 351 nm excitation of 2-nitrophenol but still above its dissociation threshold, OH quantum yield is not expected to be dependent on nitrogen carrier gas pressure.

#### **3.2.2.** Monitoring HONO and possible NO<sub>2</sub> formation from the 2-nitrophenol photolysis.

Formation of HONO and possible  $NO_2$  products from the 2-nitrophenol photolysis at 308 nm and 351 nm was investigated by comparing the 2-nitrophenol absorption spectra in the presence and absence of photolysis with the standard HONO and  $NO_2$  absorption spectra in the 364-370 nm region. Shown in Figure 6 are absorption spectra of 2-nitrophenol in the 364-370 nm region with and without photolysis at 308 nm.

A product absorption band peaking at ~368.5-369.0 nm appeared after photolyzing 2nitrophenol at 308 nm. Also displayed in Figure 6 is a standard HONO absorption spectrum recorded in the 364-370 nm region. HONO reference absorption spectrum in the 364-370 nm region was obtained by measuring the spectral absorption of the equilibrated NO<sub>2</sub>/NO/H<sub>2</sub>O/HONO mixture and subtracting the spectral absorption of the unreacted NO<sub>2</sub>. Shown in the inset is a net product spectrum after 308 nm photolysis of 2-nitrophenol and a HONO absorption spectrum in the 367.5-370.0 nm region. After comparing the net production absorption spectrum from the photolysis at 308 nm with the standard HONO spectrum, it is apparent that HONO is formed from the 2-nitrophenol photolysis at 308 nm. HONO is also a product from 2-nitrophenol photolysis at 351 nm. On the other hand, a comparison of the 2nitrophenol absorption spectra following 308 nm and 351 nm photolysis with the standard NO<sub>2</sub> spectrum indicates NO<sub>2</sub> is not formed directly from the 2-nitrophenol photolysis.

The HONO quantum yields formed from the 2-nitrophenol photolysis at 308 nm and 351

nm were determined by tuning the probe laser to HONO absorption peak around 368.5 nm and measuring the cavity losses in the absence and presence of photolysis of 2-nitrophenol at 2-nitrophenol pressures of 1.0 mTorr, 2.0 mTorr, 3.0 mTorr, and 4.0 mTorr. By dividing the HONO concentration formed from the 2-nitrophenol photolysis per photolysis pulse by the absorbed photolysis photon density, we obtained the HONO quantum yield formed from the photolysis of 2-nitrophenol at a given pressure. The HONO quantum yield was found to be



Figure 6. Cavity ring-down absorption spectra of 2.0 mTorr of 2-nitrophenol with and without 308 nm photolysis along with absorption spectra for HONO and for NO<sub>2</sub>. Spectra have been vertically shifted for ease of viewing. The spectral scan was conducted at 0.50 nm interval. Absorption by HONO standard was obtained by subtracting absorption by unreacted NO<sub>2</sub> from the measured total absorption by an equilibrated NO<sub>2</sub>/NO/H<sub>2</sub>O/HONO mixture. Shown in inset are net 2-nitrophenol photolysis product absorption spectrum, obtained by subtracting 2-nitrophenol absorption spectrum in the absence of photolysis from that in the presence of photolysis, and HONO spectrum in the 367.5-370.0 nm region.

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independent of 2-nitrophenol pressure. The average HONO quantum yields from the 308 nm and 351 nm photolysis of 2-nitrophenol are  $0.34\pm0.09$  and  $0.39\pm0.07$ , where error quoted (1 $\sigma$ ) represents experimental scatter. The magnitude of HONO yields is similar from the 308 and 351 nm photolysis of 2-nitrophenol to within the experimental error limit.

To derive HONO concentration in the HONO quantum yield measurements, HONO absorptions from 2-nitrophenol photolysis at 308 nm and 351 nm were determined by averaging absorption measurements over 10 photolysis pulses. One may ask if 308 nm and 351 nm photolysis pulses could photolyze HONO product formed in the data acquisition and data averaging processes. HONO does not have known absorption<sup>39</sup> at 308 nm. HONO is not expected to be photolyzed by the 308 nm photolysis beam. The 351 nm photon flux used in the study was low (~0.006 J/cm<sup>2</sup>), HONO absorption cross section<sup>39</sup> at 351 nm is 12 times smaller than that of 2-nitrophenol, and HONO concentration is about two orders of magnitude smaller than 2-nitrophenol concentration. Photodissociation of HONO formed by each successive 351 nm photolysis pulse is estimated to decrease HONO yield by about 0.2%. Because the effect is so small, we did not make correction to the HONO yield at 351 nm.

The dependence of HONO quantum yields on nitrogen carrier gas pressure was examined. Nitrogen pressure was varied between 20 and 600 Torr. The HONO yields from 2-nitrophenol photolysis at 308 and 351 nm were found to be independent of nitrogen pressure to within the experimental error limit.

# **3.3.** Oxidant formation rate constants from gas phase 2-nitrophenol photolysis and atmospheric implications of the results.

Atmospheric photolysis rate constant of 2-nitrophenol ( $J_{2-Nitrophenol}$ ) was calculated using the following equation:

$$J_{2\text{-Nitrophenol}} = \Sigma \sigma(\lambda) \cdot \phi(\lambda) \cdot F(\lambda) \Delta \lambda \tag{3}$$

where  $F(\lambda)$  denotes solar actinic flux,  $\sigma(\lambda)$  represents absorption cross sections of 2-nitrophenol obtained in the present study, and  $\varphi(\lambda)$  is the photolysis quantum yield for 2-nitrophenol.  $F(\lambda)\Delta\lambda$ values reported by Demeriian *et al.*<sup>53</sup> were used. Photolysis rate constants were estimated for two scenarios of photolysis quantum yields. One scenario assumes photolysis quantum yield to be unity in the 295-400 nm region. The other scenario assumes photolysis quantum yield to be unity in the 295-355 nm region and zero in the 360-400 nm region. The first scenario and the second scenario provide upper and lower limits of the 2-nitrophenol photolysis rate constant. Our experimental results have already shown that the sum of the OH and HONO quantum yields of about unity both at 308 nm and 351 nm. As OH radical was observed by laser induced fluorescence from gas phase photodissociation dynamics studies<sup>31,32</sup> of 2-nitrophenol in the 361-390 nm range, there is 2-nitrophenol photolysis in the 360-390 nm region as well. The photolysis rate constants for 2-nitrophenol were modeled as a function of the zenith angle for cloudless conditions, at sea level, and for best-estimate albedo<sup>54</sup>; they are plotted in Figure 7. The modeled photolysis rate constants for 2-nitrophenol are  $1.9 \times 10^{-2}$  to  $1.0 \times 10^{-2}$  s<sup>-1</sup> for 0-60° zenith angles at the upper limit, which translate to photolysis lifetimes of 0.9 to 1.7 min. The modeled photolysis rate constants for 2-nitrophenol are  $1.4 \times 10^{-2}$  to  $6.9 \times 10^{-3}$  s<sup>-1</sup> for 0-60° zenith angles at the lower limit, which correspond to photolysis lifetimes of 1.2 to 2.4 min. Gas phase reaction of 2-nitrophenol with OH has a reported rate constant<sup>52</sup> of  $9 \times 10^{-13}$  cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>. Using 12 h daily average OH concentration<sup>55</sup> of  $1.6 \times 10^6$  molecule cm<sup>-3</sup>, the atmospheric OH radical reaction lifetime of 2-nitrophenol is about 193 h. Even at 86° zenith angle, the modeled photolysis rate constants for 2-nitrophenol are  $6.2 \times 10^{-4}$  and  $4.0 \times 10^{-4}$  s<sup>-1</sup> at the upper and the lower limit, which correspond to photolysis lifetimes of 27 min and 42 min. Photolysis is a



Zenith angle (degree)

Figure 7. Modeled atmospheric photodissociation rate constants of 2-nitrophenol as a function of solar zenith angle under cloudless conditions, at sea level, and for best-estimate albedo. Circles: upper limit of the photolysis rate constants by assuming photolysis quantum yield of 1 in the 295-400 nm region. Squares: Lower limit of the photolysis rate constants by assuming photolysis quantum yield of 1 over the 295-355 nm range and 0 over the 360-400 nm range.

dominant gas phase degradation process for 2-nitrophenol from the atmosphere at all zenith angles. Since the oxidant formation quantum yields from 308 nm and 351 nm photolysis of 2-nitrophenol are about unity, the lower limit of oxidant formation rate constants from 2-nitrophenol gas phase photolysis are estimated in the range of  $1.4 \times 10^{-2}$  to  $6.9 \times 10^{-3}$  s<sup>-1</sup> for 0-60° zenith angles.

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The modeled 2-nitrophenol photolysis rate constant based upon current laboratory study results is two orders of magnitude faster than that of 1.4%×photolysis rate constant of NO<sub>2</sub> reported by Bardini.<sup>56</sup> For example, the upper and lower limits of our estimated 2-nitrophenol photolysis rate constants at 60° zenith angle are  $1.0\times10^{-2}$  s<sup>-1</sup> and  $6.9\times10^{-3}$  s<sup>-1</sup>. Bardini's 2-nitrophenol photolysis rate constant is about  $6.3\times10^{-5}$  s<sup>-1</sup> at 60° zenith angle. Our calculated 2-nitrophenol photolysis rates are 110-159 times faster than that reported by Bardini in 2006. The same group published<sup>25</sup> qualitative 2-nitrophenol gas phase absorption cross section data in 2011. Using the photolysis rate reported by Bardini and the 2-nitrophenol absorption cross section data from the same group would yield a 2-nitrophenol spectrally-averaged photolysis quantum yield<sup>25</sup> of 0.1%. Our direct experimental measurements of OH and HONO yields has shown the 2-nitrophenol photolysis rate constant reported by Bardini is a gross underestimate.

The modeled lower limit of HONO formation rate constant from 2-nitrophenol gas phase photolysis at 60° zenith angle using our 2-nitrophenol absorption cross section and HONO quantum yield data is about  $2.6 \times 10^{-3}$  s<sup>-1</sup>. Formation rate constant of HONO from the gas phase 2-nitrophenol photolysis of  $2.9 \times 10^{-5}$  s<sup>-1</sup> was reported<sup>6</sup> in a photo-reactor with broadband 300-500 nm irradiation by Bejan *et al*. Our calculated HONO formation rate constant from 2-nitrophenol photolysis is about two orders of magnitude faster than that reported by Bejan *et al*. The stability of the nitrophenol source varied significantly during the experiments in the literature study.<sup>6</sup> The variable and lack of calibration of absolute 2-nitrophenol concentration in air mixture in the prior study may have contributed to the large difference between the estimated HONO formation rate constant reported<sup>6</sup> by Bejan *et al*. The literature study was conducted in the time frame of several hours.

Significant HONO loss is expected when HONO formed from 2-nitrophenol photolysis was photolyzed in a photo-reactor for several hours. The OH radical formed from 2-nitrophenol photolysis could also react with HONO. These secondary losses could decrease the observed HONO concentrations and resulted in much lower HONO formation rate constant as reported in this prior study.

The importance of the gas phase 2-nitrophenol photolysis to HONO and OH formation in the atmosphere is not included in the current atmospheric chemistry model, as there was no prior quantitative laboratory near UV absorption cross section and product quantum yield information which would suggest this process to be important. Yuan et al.<sup>23</sup> measured ambient concentrations of phenol, nitrophenols (2-nitrophenol and 4-nitrophenol), methyl-nitrophenols, and dinitrophenols in the Uintah Basin, UT in winter as a result of oil and gas operations. They found phenol is mainly formed from OH radical oxidation of benzene during the daytime, while 2-nitrophenol is formed by subsequent oxidation of phenol both during the daytime and the night time. They used 2-nitrophenol photolysis rate constant<sup>56</sup> reported by Bardini in the box model simulation. But the box model cannot simultaneously fit their measured 2-nitrophenol and phenol data. If the measured phenol concentrations were used as a constraint in the box model simulation of their data, they would predict much higher nitrophenol concentrations than the measurement values. The supplement of Yuan et al. paper showed that the modeled 2nitrophenol level could be up to 150 ppt when the measured nitrophenol level is ~10-15 ppt, Given that our study has shown that the calculated 2-nitrophenol photolysis rate is much faster than that reported by Bardini, inclusion of faster 2-nitrophenol photolysis rate constant in the box model will likely reduce discrepancy in the simultaneous fitting of phenol and nitrophenol data, and explain why the modeled nitrophenol concentrations are always higher than the measurement values for both daytime and night time when 2-nitrophenol photolysis rate constant

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reported by Bardini was used. Assuming photolysis rates for nitrophenols, methyl-nitrophenols, and dinitrophenols were the same as that reported by Bardini, and assuming HONO yields were 100% from the photolysis of these compounds, Yuan et al. found the steady-state HONO concentration would only increase by 0.5 ppt in the morning and 0.2 ppt during the noontime period from the gas phase photolysis of these compounds. These additional HONO concentrations are a small fraction of the measured HONO concentrations<sup>57</sup> (50-100 ppt) during UBWOS2014, which led Yuan *et al.* to conclude that the photolysis of nitrophenols, methylnitrophenols, and dinitrophenols to be insignificant in forming HONO in the polluted atmosphere. Contrary to the conclusion by Yuan et al., if we use the calculated 2-nitrophenol photolysis rate constants determined in the current study, and the HONO yield of  $\sim 0.34$  from 2nitrophenol gas phase photolysis, and assuming photolysis rate constants and HONO quantum yields of 4-nitrophenol, methyl-nitrophenols and dinitrophenols are similar to those for 2nitrophenol, we estimated the total HONO concentration from the gas phase photolysis of nitrophenols, methyl-nitrophenols, and dinitrophenols to be around 18-26 ppt in the morning and 7-10 ppt during the noontime period. It is not difficult to see that HONO formation from the gas phase photolysis of these nitrophenol compounds can account for a significant fraction of the HONO concentration in the UBWOS 2014. The co-product of the HONO formation channel from the gas phase 2-nitrophenol photolysis can extract an H-atom to form phenoxy radical  $(C_6H_5O_{\bullet})$ ; subsequent reaction<sup>58</sup> of phenoxy radical with NO<sub>2</sub> in the atmosphere can regenerate 2-nitrophenol. Results of the present laboratory study highlight the importance of 2-nitrophenol photolysis in the formation of OH and HONO in the atmosphere. Its contribution to the oxidation capacity of the atmosphere should not be overlooked.

In addition to gas phase degradation processes, wet deposition is generally thought to

play an important role in the removal of nitrophenol compounds from the atmosphere. The partition between the atmospheric gas and the liquid phase is different for different nitrophenols. For example, 2-nitrophenol is much more hydrophobic than 4-nitrophenol,<sup>59</sup> which can displace 2-nitrophenol towards the gas phase and leave the less volatile 4-nitrophenol being preferentially present in the aqueous phase.<sup>7,21,22</sup> For 2-nitrophenol, its Henry's law constant in the aqueous phase<sup>59</sup> is small (81 M atm<sup>-1</sup> at 298 K). For a typical tropospheric cloud water volume fraction of ~10<sup>-6</sup> at ~280 K, an equilibrium partitioning of ~1% into the aqueous phase is predicted from the Henry's Law coefficient for 2-nitrophenol. Given that the current study indicates that gas phase 2-nitrophenol photolysis is several orders of magnitude faster than its reaction with OH radical in the gas phase, 2-nitrophenol gas phase photolysis is likely much more important in removing 2-nitrophenol from the atmosphere than its aqueous phase removal.

#### Conclusions

2-Nitrophenol is an important component of "brown carbon" in the atmosphere. The concentration of 2-nitrophenol is expected to be high in polluted urban areas where there are increased emissions of aromatic hydrocarbons. To assess the air quality impacts of pollutant emission, it is important to know oxidant formation potential of the emitted species. Although photodissociation dynamics studies<sup>31,32</sup> of 2-nitrophenol have reported OH formation at photolysis wavelengths of 266 nm, 355 nm, and over the 361-390 nm range, and HONO was observed as a product<sup>6</sup> from 2-nitrophenol photolysis in smog chamber, the lack of quantitative absorption cross section and product quantum yield information has prevented quantitative assessment of the extent of oxidant formation from 2-nitrophenol photolysis in the atmosphere. The current work has served the purpose of filling this missing knowledge gap, without which the importance of the gas phase photolysis of 2-nitrophenol in the formation of atmospheric

oxidants cannot be assessed with any certainty. Given that there are multitudes of pollutants in the atmosphere and there are many factors that could affect ambient oxidant concentrations, it is often difficult to identify important processes that contribute to atmospheric oxidant formation based upon field study results alone. Our experimental work has demonstrated why careful laboratory studies are still needed to address the complex problem of atmospheric oxidant formation.

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