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### Gas-phase absorption cross sections of 2-nitrobenzaldehyde and benzaldehyde in the 285–400 nm region, and photolysis of 2-nitrobenzaldehyde vapor at 308 and 351 nm

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### ABSTRACT

We have measured the gas-phase absorption cross sections of 2-nitrobenzaldehyde and benzaldehyde in the 285–400 nm region by using cavity ring-down spectroscopy (CRD). Absorption cross sections of 2nitrobenzaldehyde vapor at 290 and 400 nm are 10.7-fold and 5.5-fold lower than 2-nitrobenzaldehyde aqueous-phase cross section values. The HCO and the NO<sub>2</sub> product channels, after 308 and 351 nm photolysis of 2-nitrobenzaldehyde vapor, were examined. Neither HCO nor NO<sub>2</sub> was detected. Upper limits for the HCO and NO<sub>2</sub> quantum yields are  $\leq 2.2\%$  and  $\leq 6.4\%$  at 308 nm, respectively. Preliminary end-product study indicates that 2-nitrobenzaldehyde photodissociates at 308 nm but not at 351 nm. © 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

2-Nitrobenzaldehyde (also called o-nitrobenzaldehyde; o- $C_6H_4(NO_2)CHO$ ) has been detected as a product of the oxidation of toluene in a  $NO_x$ -rich atmosphere [1]. It is used in the preparation of dyes, pesticides, non-linear optical materials, and pharmaceutical drugs [2], and is toxic. 2-Nitrobenzaldehyde has been used successfully as an actinometer in photochemical studies [3,4]. It can undergo photoisomerization to form *o*-nitrosobenzoic acid, with a quantum yield of 0.5 in the 300–410 nm region in both the liquid and solid phases [3,5,6]. The mechanism for the photoisomerization of 2-nitrobenzaldehyde in the aqueous-phase has been postulated to involve a transient ketene [7] or a short-lived triplet intermediate [8]. The UV/visible absorption spectrum of 2nitrobenzaldehyde has been measured in non-polar solvents [9,10] in the 290–420 nm region. Due to the compound's low vapor pressure (~0.003 Torr at 298 K), the gas-phase absorption cross sections, the photolysis product channels and quantum yields of 2-nitrobenzaldehyde vapor have not been determined. Since removal of 2-nitrobenzaldehyde by tropospheric gas-phase photochemistry is a highly probable process, further work is needed to evaluate the potential importance of photolysis.

The photolysis of 2-nitrobenzaldehyde can occur through the following pathways:

$$p-C_6H_4(NO_2)CHO + h\nu \rightarrow o-C_6H_4(NO)COOH$$
 (R1)

$$\rightarrow C_6 H_4 CHO + NO_2 \quad (\lambda \le 403 \text{ nm}) \qquad (\text{R2})$$

$$\rightarrow C_6 H_4 NO_2 + HCO \quad (\lambda \le 326 \text{ nm}) \qquad (R3)$$

$$\rightarrow C_6 H_5 NO_2 + CO \quad (\lambda \le 600 \text{ nm}) \tag{R4}$$

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where photochemical thresholds were calculated from the corresponding bond energy changes. Pathway (R1) is an intramolecular photoisomerization channel. Pathway (R2) is an NO<sub>2</sub> formation channel. Pathway (R3) is a radical formation channel. Pathway (R4) is a molecular elimination channel.

In this Letter, we report results obtained from absorption cross section measurements of 2-nitrobenzaldehyde in the 285–400 nm region. Absorption cross sections of benzaldehyde have also been measured over the same wavelength range for comparative purposes. We searched for possible HCO and NO<sub>2</sub> products from 308 and 351 nm photolysis of 2-nitrobenzaldehyde by using excimer laser photolysis combined with cavity ring-down spectroscopy [11,12]. Neither HCO nor NO<sub>2</sub> was detected. We have estimated the atmospheric photolysis rate constants of 2-nitrobenzaldehyde vapor using the gas-phase absorption cross section data of 2-nitrobenzaldehyde determined in this work.

### 2. Experimental

The gas-phase absorption cross sections of 2-nitrobenzaldehyde and benzaldehyde in the 285–400 nm region were measured in a 50 cm long cell by cavity ring-down spectroscopy [11,12]. A pair of highly reflective cavity mirrors vacuum-seal the two ends of the cell. Four pairs of high-reflectance cavity mirrors with centering wavelengths at 285, 310 nm (covering 290–330 nm region), 320 nm (covering 300–340 nm region), and 375 nm (covering 340–400 nm region) were used in the cross section measurements. The fundamental or the second harmonic output from a XeCl excimer-pumped dye laser (at a much reduced fluence level) was transmitted into the ring-down cavity through the front cavity mirror. The laser dyes used to cover the 285–400 nm region were





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coumarin 153, rhodamine 6G, rhodamine B, DCM, PTP, and BBQ, The photon intensity decay inside the cavity was monitored by a photomultiplier tube (PMT) inserted behind the rear cavity mirror. The PMT output was amplified, digitized, and transferred to a computer. The decay curve was fitted to a single-exponential decay function, from which the ring-down time constant ( $\tau$ ) and the total loss ( $\Gamma$ ) per optical pass were calculated. When cavity mirrors were properly aligned, the maximum uncertainty for fitting the ringdown decay curve to a single-exponential decay function was 5%. Optical loss due to absorption by 2-nitrobenzaldehyde vapor was determined through measurement of the cavity losses with and without 2-nitrobenzaldehyde in the cavity. Ring-down decay times for an empty cavity were about 0.31 µs at 285 nm, 0.95 µs at 310 nm, 1.19 µs at 320 nm, and 2.71 µs at 375 nm. With 2-nitrobenzaldehyde vapor in the cavity, ring-down decay times shortened to as short as 0.21 us at 285 nm. 0.53 us at 310 nm. 0.76 us at 320 nm, and 2.05 us at 375 nm. The gas pressure inside the cell was read by an MKS Baratron capacitance manometer (1 Torr full scale), which can measure pressures down to  $10^{-4}$  Torr (pressure measurement accuracy is about 25% at 0.4 mTorr, 10% at 1 mTorr, and 5% at 2 mTorr). The cell was evacuated to  $10^{-5}$  Torr (measured with a cold cathode vacuum gauge) with a combination of rotary and diffusion pumps before each experiment. The cell had an outgassing rate of  $5 \times 10^{-5}$  Torr/min. For absorption cross section measurements, 2-nitrobenzaldehyde pressure inside the cell was varied between  $4 \times 10^{-4}$  Torr and  $2 \times 10^{-3}$  Torr; absorptions of the probe beam by 2-nitrobenzaldehyde at six different pressures were measured for each cross section run. The cell was pumped out before 2-nitrobenzaldehyde at a different pressure was allowed to flow into the cell, so as to minimize the effect of outgassing. The cross section measurements were made under static condition. It took up to 4 min for  $2 \times 10^{-3}$  Torr of 2-nitrobenzaldehyde to fill the cell. Once the cell was filled with a sample, about 8 s were needed to perform a ring-down measurement, with a laser repetition rate of 1 Hz and with 8 count average. With the cell degassing rate and the sample filling time as well as the accuracy of the pressure read-out taken into account, the uncertainty in the 2-nitrobenzaldehvde concentration measurements is  $\leq 35\%$  at  $4 \times 10^{-4}$  Torr,  $\leq 20\%$  at  $1 \times 10^{-3}$  Torr, and  $\leq 15\%$  at  $2 \times 10^{-3}$  Torr. Benzaldehyde absorption cross section measurements were made under static conditions for all wavelengths except 285 nm; at that wavelength, the cross section measurement was made under slowflow condition. Absorptions of the probe beam by benzaldehyde at six different pressures were determined for each cross section run. The vapor pressure of benzaldehyde is about 0.85 Torr at room temperature. Pressure measurement uncertainty due to outgassing can be neglected, since the benzaldehyde sample quickly filled the cell. Pressures of benzaldehyde used in the cross section measurements ranged from 0.6-2.3 mTorr at 285 nm to 0.22-0.83 Torr at 400 nm. The maximum uncertainty in the determination of the benzaldehyde concentration was about 17% at 285 nm, and about 1% at 400 nm.

Photolysis of 2-nitrobenzaldehyde occurred in a stainless steel cell. Detailed descriptions about our experimental setup can be found elsewhere [13–15]. The output from an excimer laser was directed into the reaction cell at an angle of  $15^{\circ}$  to the main cell axis, through a side arm. The probe laser beam, used to monitor NO<sub>2</sub> and HCO generated from the photolysis process, entered the cell along the main cell axis. The cell had been vacuum-sealed with a pair of highly reflective cavity mirrors. The probe laser beam overlapped with the photolysis beam at the center of the cavity. The photolysis/probe laser overlap region can be envisioned as a rectangular solid with its center overlapping that of the cell, with its width and height defined by those of the photolysis beam, and with its length defined by (beam width) × (tan  $15^{\circ}$ )<sup>-1</sup>, where  $15^{\circ}$  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)  $\times$  (sin 15°)<sup>-1</sup>. For a 12 mm wide photolysis beam, the length of the photolysis/probe laser overlap region is about 4.6 cm. We probed for the NO<sub>2</sub> product from the photolysis of 2-nitrobenzalde-hyde in the 439–448 nm region, and we probed for the HCO product from the photolysis of 2-nitrobenzaldehyde in the 613–617 nm region (HCO X<sup>2</sup>A" (0, 0, 0)  $\rightarrow$  A<sup>2</sup>A' (0, 9, 0) transition). A pulse/delay generator was used to vary the delay time between the firings of the photolysis laser and the probe laser. The end-products from the 308 nm photolysis of 2-nitrobenzaldehyde were quantified using a Fourier-transform infrared spectrometer (Bruker IFS 66v).

2-Nitrobenzaldehyde is a light-yellow fine crystal at 295 K, and was obtained from Aldrich ( $\ge$ 98% purity). It was pumped overnight and stored in a gas bulb. 2-Nitrobenzaldehyde in the gas bulb was pumped for at least 30 min before being introduced into the cell. Displayed in Fig. 1 is an IR absorption spectrum of 2-nitrobenzaldehyde vapor in the 500–3500 cm<sup>-1</sup> region (0.5 cm<sup>-1</sup> resolution). Benzaldehyde is a liquid at 295 K and was obtained from Aldrich ( $\ge$ 99.5% purity). All experiments were carried out at an ambient temperature of 295 ± 2 K.

#### 3. Results and discussion

### 3.1. Absorption cross sections of 2-nitrobenzaldehyde vapor in the 285–400 nm region

We have determined the gas-phase UV absorption cross section of 2-nitrobenzaldehyde in the 285-400 nm region by use of cavity ring-down spectroscopy. The validity of using cavity ring-down spectroscopy for accurate cross section determination of low vapor pressure compound has been demonstrated in our recent work [16], in which we measured absorption cross section of E.E-2.4hexadienedial (HCO-CH=CH-CH=CH-CHO) in the 290-430 nm region. The room temperature vapor pressure of E,E-2,4-hexadienedial is ~4 mTorr, comparable in magnitude to the room temperature vapor pressure of 2-nitrobenzaldehyde. The cross section values of E,E-2,4-hexadienedial in the 315–345 nm region determined using ring-down technique agree with cross section values of E,E-2,4-hexadienal (CH3-CH=CH-CH=CH-CHO) determined using diode-array spectrometer [17] to within 10%. The near UV/visible band of E.E-2,4-hexadienedial is broader than that of E,E-2,4-hexadienal, and the cross section data of E,E-2,4-hexadienedial obtained using ring-down technique in the 350-400 nm region are larger than cross section data of E,E-2,4-hexadienal since the  $n \rightarrow \pi^*$  transitions arise from symmetric and antisymmetric combinations of the n(0) orbitals on the two carbonyl centers for



Fig. 1. FTIR spectrum of 2 mTorr of 2-nitrobenzaldehyde vapor.

Table 1

E,E-2,4-hexadienedial. In the present study, absorption cross section of 2-nitrobenzaldehyde at each wavelength was determined by measurement of the round-trip cavity losses due to absorption as a function of 2-nitrobenzaldehyde pressure in the cavity, plotting of the absorption against 2-nitrobenzaldehyde pressure, and extraction of the absorption cross section from the slope of the plot. Fig. 2 shows round-trip absorption plotted against 2-nitrobenzaldehvde pressure at 350 nm. 2-Nitrobenzaldehvde absorption cross section of  $1.78\times 10^{-19}\,cm^2/molecule$  was derived from the slope of the plot. 2-Nitrobenzaldehyde gas-phase absorption cross section at each wavelength was independently measured for 3–8 times. Cross section values for 2-nitrobenzaldehyde vapor as a function of wavelength thus obtained are listed in Table 1 and shown in Fig. 3. The absorption spectrum of 2-nitrobenzaldehyde in the 285–400 nm region could originate from several  $n \rightarrow \pi^*$ transitions [10] from the lone pairs of nitro and aldehyde groups into  $\pi^*$  orbitals localized either in the benzene ring or in the NO<sub>2</sub> and CHO moieties. The errors quoted  $(1\sigma)$  represent the estimated precision of cross section measurements obtained from the standard deviation of 3-8 cross section measurements. Systematic uncertainties in the cross section data arise mainly from errors in pressure measurements (up to 35-17% for 2-nitrobenzaldehyde pressure in the  $4 \times 10^{-4}$ -2  $\times 10^{-3}$  Torr range) and to a lesser extent from errors in the determination of absorption (5%). The relative absorption cross sections as a function of wavelength are determined more accurately than the absolute cross section values as many of the systematic errors are about the same for the measurements made at different wavelengths. With both random errors and systematic errors taken into account, the overall uncertainties in the determination of 2-nitrobenzaldehyde cross sections are 40% at 290 and 345 nm; 45% at 285, 350, 355, 365, 390 nm, and in the 305-315 nm and 325-335 nm regions; 50% at 295, 300, 320, 340, 360, 370, 375, 385, and 400 nm; and 55% at 380 and 395 nm. Cross section values of 2-nitrobenzaldehyde vapor in the 285–400 nm region range from  $1.04 \times 10^{-18}$  to  $1.80 \times 10^{-20}$  cm<sup>2</sup>/molecule.

Shown in Fig. 3 for comparison are previously reported aqueous-phase absorption cross sections of 2-nitrobenzaldehyde [9] in non-polar solvents in the 290–400 nm region. The aqueousphase absorption cross sections of 2-nitrobenzaldehyde ranged from  $6.39 \times 10^{-18}$  cm<sup>2</sup>/molecule at 290 nm to  $9.90 \times 10^{-20}$  cm<sup>2</sup>/ molecule at 400 nm. The gas-phase absorption cross sections of 2-nitrobenzaldehyde determined in our study ranged from



**Fig. 2.** Round-trip absorption (base e) plotted against 2-nitrobenzaldehyde pressure at 350 nm. The solid line is a linear least-squares fit of the data points. An absorption cross section of  $1.78 \times 10^{-19} \, cm^2$ /molecule was derived from the slope of the plot.

Absorption cross sections ( $\sigma$ , in units of cm<sup>2</sup>/molecule, base e) of 2-nitrobenzaldehyde (2-NBA) and benzaldehyde (BA) as a function of wavelength ( $\lambda$ ).

λ	σ	σ
(nm)	(cm <sup>2</sup> /molecule, 2-NBA)	(cm <sup>2</sup> /molecule, BA)
285	$(1.04\pm 0.05^{a,b})\times 10^{-18}$	$(2.12 \pm 0.01^{a,c}) \times 10^{-13}$
290	$(5.98 \pm 0.01)  imes 10^{-19}$	$(9.01 \pm 0.06) \times 10^{-20}$
295	$(3.31 \pm 0.23)  imes 10^{-19}$	$(4.61 \pm 0.09) \times 10^{-20}$
300	$(3.11 \pm 0.21) \times 10^{-19}$	$(3.85 \pm 0.16) \times 10^{-20}$
305	$(3.10 \pm 0.17) \times 10^{-19}$	$(5.18 \pm 0.07) \times 10^{-20}$
310	$(3.03 \pm 0.12) \times 10^{-19}$	$(4.50 \pm 0.05) \times 10^{-20}$
315	$(2.67 \pm 0.04)  imes 10^{-19}$	$(6.06 \pm 0.42) \times 10^{-20}$
320	$(2.07 \pm 0.21) \times 10^{-19}$	$(5.71 \pm 0.32) \times 10^{-20}$
325	$(2.00 \pm 0.07)  imes 10^{-19}$	$(5.98 \pm 0.06) \times 10^{-20}$
330	$(2.08 \pm 0.06) \times 10^{-19}$	$(7.23 \pm 0.51) \times 10^{-20}$
335	$(1.98 \pm 0.10) \times 10^{-19}$	$(6.03 \pm 0.07) \times 10^{-20}$
340	$(1.92 \pm 0.16) \times 10^{-19}$	$(6.94 \pm 0.08) \times 10^{-20}$
345	$(1.82 \pm 0.01) \times 10^{-19}$	$(5.71 \pm 0.12) \times 10^{-20}$
350	$(1.78 \pm 0.05)  imes 10^{-19}$	$(3.65 \pm 0.11) \times 10^{-20}$
355	$(1.50 \pm 0.08) \times 10^{-19}$	$(4.60 \pm 0.04) \times 10^{-20}$
360	$(1.34 \pm 0.10) \times 10^{-19}$	$(6.95 \pm 0.18) \times 10^{-20}$
365	$(1.21 \pm 0.06) \times 10^{-19}$	$(5.96 \pm 0.15) \times 10^{-20}$
370	$(8.28 \pm 0.48) \times 10^{-20}$	$(1.30 \pm 0.02) \times 10^{-20}$
375	$(6.65 \pm 0.55) \times 10^{-20}$	$(4.28 \pm 0.05) \times 10^{-21}$
380	$(5.12 \pm 0.57) \times 10^{-20}$	$(7.36 \pm 0.04) \times 10^{-22}$
385	$(4.36 \pm 0.32) \times 10^{-20}$	$(2.36 \pm 0.04) \times 10^{-22}$
390	$(2.85 \pm 0.03) \times 10^{-20}$	$(1.02 \pm 0.04) \times 10^{-22}$
395	$(2.35 \pm 0.27) \times 10^{-20}$	$(2.46 \pm 0.01) \times 10^{-22}$
400	$(1.80 \pm 0.10) \times 10^{-20}$	$(7.06 \pm 0.48) \times 10^{-23}$

Errors quoted are standard deviations in the precision of the measurements.

<sup>b</sup> The overall uncertainties in the determination of 2-nitrobenzaldehyde cross sections are 40% at 290 and 345 nm; 45% at 285, 350, 355, 365, 390 nm, and in the 305–315 nm and 325–335 nm regions; 50% at 295, 300, 320, 340, 360, 370, 375, 385, and 400 nm; and 55% at 380 and 395 nm.

<sup>c</sup> The overall uncertainties in the determination of benzaldehyde cross sections are 10% in the 290–310 nm, 335–345 nm, 355–365 nm, and 380–395 nm region, and at 325 and 375 nm; 15% at 315, 320, 350, 370, and 400 nm; 20% at 330 nm; and 25% at 285 nm.



**Fig. 3.** Absorption cross sections of 2-nitrobenzaldehyde in the 285–400 nm region. Circles represent gas-phase cross section data determined in this work. Precision of the measurement is shown for all wavelengths. Absolute error bars are shown for data points at 285 and at 350 nm. Solid line represents aqueous-phase cross section data obtained for 2-nitrobenzaldehyde in non-polar solvents [9].

 $5.98 \times 10^{-19}$  cm<sup>2</sup>/molecule at 290 nm to  $1.80 \times 10^{-20}$  cm<sup>2</sup>/molecule at 400 nm. The liquid-phase absorption cross sections of 2nitrobenzaldehyde at 290 and 400 nm are 10.7-fold and 5.5-fold greater than those in the gas-phase. The difference between the liquid-phase and gas-phase UV absorption cross sections of 2-nitrobenzaldehyde can be partially attributed to the red shift of the liquid-phase absorption spectrum of 2-nitrobenzaldehyde, compared with the gas-phase spectrum. Solution-phase cross section data have been used to model the gas-phase photolysis of 2-nitrobenzaldehyde since gas-phase spectroscopic information in the UV/visible region are lacking [18]. Our current data show a large difference exists between the gas-phase and aqueous-phase UV absorption cross sections of 2-nitrobenzaldehyde. Thus, only gasphase cross section data should be used to model the gas-phase photolysis of 2-nitrobenzaldehyde.

# 3.2. Comparison between gas-phase absorption cross section values of 2-nitrobenzaldehyde and of benzaldehyde, in the 285–400 nm region

We have determined the gas-phase absorption cross sections of benzaldehyde in the 285-400 nm region, in order to compare them with the cross section data of 2-nitrobenzaldehyde. The benzaldehyde cross section data determined in this study are listed in Table 1. The errors quoted  $(1\sigma)$  are the estimated precision of cross section measurements obtained from the standard deviation of at least three independent cross section measurements. With both random errors and systematic errors taken into account, the overall uncertainties in the determination of benzaldehyde cross sections are 10% in the 290-310 nm, 335-345 nm, 355-365 nm, and 380-395 nm region, and at 325 and 375 nm; 15% at 315, 320, 350, 370, and 400 nm; 20% at 330 nm; and 25% at 285 nm. Displayed in Fig. 4 are UV absorption cross sections of 2-nitrobenzaldehyde and benzaldehyde as a function of wavelength. In addition to the gas-phase benzaldehyde cross section data determined in this study, previously reported benzaldehyde cross section values of Thiault et al. [19], of Zhu and Cronin [20], and of Nozière et al. [21] are included. Our benzaldehyde cross section data agreed with those obtained by Thiault et al. to within 5% at 320 nm; to within 15% in the 305-315 nm region and at 325 nm; to within 20% at 300 nm and in the 330-340 nm region; to within 25% at 295 nm; to within 30% at 285 nm; to within 35% at 345 and 355 nm; to within 40% at 290 nm; and to within 45% at 350 nm. Our benzaldehyde cross section data at 360 and 365 nm are 2.9-fold and 2.5-fold greater than the cross section values reported by Thiault et al. The cross section data obtained by Thiault et al. in the 345-365 nm region appear to be limited by detection sensitivity of the diode-array spectrometer that was used. Zhu and Cronin [20] previously determined absorption cross sections of benzaldehyde, by varying benzaldehyde pressure in the cell and monitoring the corresponding



**Fig. 4.** Gas-phase absorption cross sections of 2-nitrobenzaldehyde and benzaldehyde in the 285–400 nm region. Circles represent 2-nitrobenzaldehyde cross section data determined in this work. Benzaldehyde cross section data included in the figure are those obtained by Zhu and Cronin [20] (hexagons), by Thiault et al. [19] (solid line), by Nozière et al. [21] (diamonds), and in this work (triangles).

changes in the photolysis fluence transmitted through the cell; they reported benzaldehyde cross section values of  $1.8 \times 10^{-19}$  $3.2 \times 10^{-19}$ , and  $3.8 \times 10^{-20}$  cm<sup>2</sup>/molecule at 280, 285, and 308 nm, respectively. The benzaldehyde absorption cross section reported in the present work agrees to within 20% with the one reported by Zhu and Cronin [20] at 308 nm. However, at 285 nm, the benzaldehyde absorption cross section determined in the present work is 6.6-fold greater than that reported by Zhu and Cronin. This disparity likely results from the combination of the low vapor pressure of benzaldehyde (~0.85 Torr at 295 K) and the use of an insensitive transmitted photolysis fluence measurements to determine benzaldehyde absorption cross sections in the previous study. Thus, the benzaldehyde cross section data reported here supersede the previous cross section data reported by our group. Nozière et al. [21] obtained benzaldehyde cross section values of  $2.1 \times 10^{-18}$ and  $1.65 \times 10^{-18} \text{ cm}^2/\text{molecule}$  at 290 and 300 nm, respectively. The benzaldehvde cross section data at 290 and 300 nm determined in the present study are 23.3-fold and 42.9-fold lower than those reported by Nozière et al. [21]. Such a disparity probably resulted from the presence of absorbing benzaldehyde photolysis products in the study of Nozière et al.

A comparison of the UV absorption spectra of benzaldehyde and 2-nitrobenzaldehyde in the 285–400 nm range shows that (i) the UV absorption spectrum of 2-nitrobenzaldehyde is broader than that of benzaldehyde; and (ii) the absorption cross sections of 2-nitrobenzaldehyde are larger than those of benzaldehyde in this region. Both characteristics could result from the contribution of an additional NO<sub>2</sub> moiety to the conjugated  $\pi$  system of benzaldehyde.

# 3.3. Time-resolved studies of the photolysis of 2-nitrobenzaldehyde at 308 and 351 nm

We investigated the photolysis of 2-nitrobenzaldehyde at 308 and 351 nm by probing for possible photodissociation products, such as HCO and NO<sub>2</sub>, immediately after the photolysis process. We probed for the HCO radical in the 613–617 nm region (HCO  $X^2A''$  (0, 0, 0)  $\rightarrow A^2A'$  (0, 9, 0) transition), and for NO<sub>2</sub> product in the 439–448 nm region. However, neither HCO nor NO<sub>2</sub> was detected after 308 nm or 351 nm photolysis of 2-nitrobenzaldehyde.



**Fig. 5.** Estimated atmospheric photolysis rate constants of 2-nitrobenzaldehyde as a function of solar zenith angle under cloudless conditions, at sea level, and for best-estimate albedo. At a solar time of 12:00 p.m. and at a latitude of 40°N, the solar zenith angle [22] is 63.0° on January 1 and 16.9° on July 1.

Since our preliminary end-product study indicates that 2-nitrobenzaldehyde vapor was not photolyzed at 351 nm, we provide here the estimated maximum HCO and  $NO_2$  quantum yields after 308 nm photolysis of 2-nitrobenzaldehyde.

The minimum round-trip HCO absorption that can be detected with our current cavity ring-down setup is 1 ppm. The length of the photolysis/probe laser overlap region is 4.6 cm, with a 12 mm wide excimer beam. With an HCO absorption cross section [14] of  $\sim 2.0 \times 10^{-18}$  cm<sup>2</sup>/molecule at 613.80 nm (R bandhead), the absence of detectable levels of HCO at the 308 nm photolysis wavelength suggests that the HCO concentration in the photolysis/ probe laser overlap region was lower than  $5.4 \times 10^{10}$  molecules/ cm<sup>3</sup>. The absorbed photon density from 308 nm photolysis of 0.003 Torr 2-nitrobenzaldehyde was about  $2.5 \times 10^{12}$  molecules/ cm<sup>3</sup>, with an incident photolysis fluence of about 0.055 I/cm<sup>2</sup> at this wavelength. The lack of detection of HCO at 308 nm suggests that the upper limit for the HCO guantum yield is below 2.2% at this wavelength. A similar calculation suggests that the maximum NO<sub>2</sub> quantum yield from 308 nm photolysis of 2-nitrobenzaldehyde is 6.4%. The estimated maximum HCO quantum yield from the 308 nm photolysis of 2-nitrobenzaldehyde, 2.2%, is much smaller than the HCO quantum yield of 29% reported previously by our group [20] for the 308 nm photolysis of benzaldehyde.

# 3.4. Atmospheric photolysis rate constant of 2-nitrobenzaldehyde vapor

We have estimated the atmospheric photolysis rate constants  $(k_{photolysis})$  of 2-nitrobenzaldehyde vapor with the following formula:

$$k_{photolysis} = \sum \sigma(\lambda) \cdot \varphi(\lambda) \cdot J(\lambda) \Delta \lambda$$

where  $J(\lambda)$  represents actinic solar flux,  $\sigma(\lambda)$  represents the gasphase absorption cross sections of 2-nitrobenzaldehyde determined in this work, and  $\varphi(\lambda)$  represents the photolysis quantum yield for 2-nitrobenzaldehyde.  $J(\lambda)\Delta\lambda$  values reported by Demerjian et al. [22] were used. In the photolysis rate calculation,  $\varphi(\lambda)$  was assumed to be unity in the 290-310 nm region, and 0 at 350 nm; in the 310-350 nm region,  $\varphi(\lambda)$  was assumed to decrease linearly, from 1 at 310 nm to 0 at 350 nm. (Our preliminary end-product study indicates that 2-nitrobenzaldehyde photodissociates at 308 nm with a photolysis quantum yield of about unity. Our end-product study also indicates that 2-nitrobenzaldehyde vapor does not undergo photodissociation at 351 nm photolysis wavelength.) Note that  $\varphi(\lambda)$  may not actually vary linearly with wavelength in the 310– 350 nm region; we made this assumption solely to simplify the photolysis rate estimation. The photolysis rate constants for 2nitrobenzaldehyde were estimated as a function of the zenith angle under cloudless conditions, at sea level, and for best-estimate albedo [23] (5% in the 290-350 nm region); the results are shown in Fig. 5. Our estimated photolysis rate constants for 2-nitrobenzaldehyde for zenith angles in the 0–60° range are  $5.6 \times 10^{-4}$  to  $2.3 \times 10^{-4}$  s<sup>-1</sup>; these values correspond to photolysis lifetimes of 0.5–1.2 h. The rate constant for reaction of 2-nitrobenzaldehyde vapor with OH or with NO<sub>3</sub> radical has not been previously reported. Assuming the OH/2-nitrobenzaldehyde and the NO<sub>3</sub>/2-nitrobenzaldehyde reaction rate constants are the same as rate constants for the OH/benzaldehyde and NO<sub>3</sub>/benzaldehyde reactions [24] ( $k_{OH+benzaldehyde} = 1.4 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>,  $k_{NO3+benzaldehyde} = 4.3 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) and using 12 h daily average OH concentration [25] of  $1.6 \times 10^{6}$  molecule/cm<sup>3</sup> and an average NO<sub>3</sub> concentration [26] of  $5 \times 10^{8}$  molecule/cm<sup>3</sup>, the tropospheric lifetimes of 2-nitrobenzaldehyde vapor due to reaction with OH and NO<sub>3</sub> are about 12.4 h and 5.4 days. Photolysis is a major process for removing 2-nitrobenzaldehyde from the atmosphere.

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