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2-Nitrobenzaldehyde as a chemical actinometer for solution and ice photochemistry

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ABSTRACT

2-Nitrobenzaldehyde (2NB) is a convenient, photochemically sensitive, and thermally robust actinometer. Although 2NB has been used in a number of solution and ice experiments in the laboratory, the quantum efficiencies and molar absorptivities of 2NB have not been critically evaluated, especially on ice. Using a series of laboratory and field measurements we have measured the light absorbance and photochemical properties of 2-nitrobenzaldehyde in solution (water and/or acetonitrile) and in/on water ice. Our results show that the molar absorptivities of 2NB are only weakly dependent upon temperature and that the quantum yield is independent of temperature in water; the quantum yield is also independent of wavelength, as shown by past reports. Furthermore, we find that the photochemistry of 2NB in/on water ice is the same as in liquid water. While most studies employing 2NB cite and use a quantum yield of 0.50, based on a review of the literature, and on our new experimental data, we recommend a quantum yield of 0.41 for 2NB photolysis for both solution and water ice.

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1. Introduction

Chemical actinometers are used to determine photon fluxes by measuring either the rate of actinometer loss and/or the formation of photoproduct(s). The ideal chemical actinometer is thermally stable, has relatively simple (and understood) photochemistry over a wide range of wavelengths, is easily analyzed, and is unaffected by its photoproducts [1]. 2-Nitrobenzaldehyde (2NB) fits this description: it is a rapid, simple actinometer that undergoes intramolecular photoisomerization to primarily produce 2-nitrosobenzoic acid [2,3]. This first-order phototransformation was first described over a century ago by Ciamician and Silber [4]. Since this time, 2NB has been used in a myriad of studies to determine ambient actinic fluxes or to scale results from laboratory illumination systems to ambient sunlight conditions. For example, 2NB has been used to: (1) measure relative photon fluxes in the ambient atmosphere [2]; (2) measure UV extinction in tropical marine waters [5]; (3) normalize oxidant formation rates during simulated sunlight illumination of cloud and fog waters in the laboratory to ambient sunlight [6–8]; (4) scale drug photostability test results from lab to ambient sun [9]; and (5) validate a snowpack radiation transfer model [3]. Similarly, 2NB has been used to measure photon fluxes in laboratory ice samples in order to determine quantum efficiencies for the photolysis of chromophores such as nitrate and nitrite [10–12].

In some actinometric applications, such as quantifying photon fluxes during monochromatic illumination, using 2NB requires knowledge of its molar absorptivities and quantum yield. Though room temperature molar absorptivities of 2NB have been reported [3,6–9,13,14], the effect of temperature has not been examined. Furthermore, while the quantum yield for 2NB photodegradation is typically taken as 0.50 in both solution- and solid-phase studies [1,2,10,15,16], there has been no evaluation of the available data, no study of the effect of temperature on the quantum yield, and no measurements of 2NB photolysis in/on water ice. These latter measurements are especially important given the growing interest in photochemical processes in deposited snow and ice [17].

The goal of this study is to more fully characterize the light absorbance and photochemistry of 2-nitrobenzaldehyde. Specifically, here we: (1) report molar absorptivities for aqueous 2NB over a range of wavelengths and temperature, (2) compile and discuss the available data for 2NB photolysis in solution and as a solid, (3) experimentally examine the temperature-dependence for 2NB photolysis, (4) determine the quantum yield for 2NB photodegradation in acetonitrile and in/on water ice, and (5) report on the use of 2NB as an actinometer in snow in the field.

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2. Experimental

2.1. Chemicals and solutions

Acetonitrile (99.9%; HPLC grade) was from Fisher, while 2NB (98%) was from Aldrich and was used as received. Deionized purified water ("Milli-Q", ≥18.2 MΩ cm) was obtained from a Milli-Q system (Millipore), fed with either melted snow (while in the field) or deionized water (in the lab). 2NB solutions (10 μM) were made in Milli-Q water (or in Milli-Q and acetonitrile) without adjusting (or measuring) the pH. 2NB solid and solutions were kept in the dark when not in use; there was no decay of 2-nitrobenzaldehyde in the dark, whether in solution or in ice.

2.2. Molar absorptivities

Absorbance spectra in water were measured for a Milli-Q blank and five aqueous solutions of 2NB (0.25–9.27 mM) using a Shimadzu UV-2501PC spectrophotometer with 1.0 cm FUV cuvettes (Spectrocell) and Milli-Q as a reference. The temperature of the sample and reference cuvettes was controlled by circulating Milli-Q from a Neslab RTE-211 water bath through the walls of the cuvette holder. The base-10 molar absorptivity at each wavelength ($\varepsilon_{2NB,\lambda}$, M^{-1} cm^{-1}) was calculated as the slope of a linear regression of measured absorbance versus the product of 2NB concentration and cuvette path length. Molar absorptivities in acetonitrile/water solutions at 313 nm were calculated from Beer's law using the measured absorbance of a 25 μM 2NB solution in a 5-cm FUV cuvette with the same acetonitrile/water mixture in the reference cell.

2.3. Illumination of 2NB in the laboratory

The photodegradation of 2NB with simulated sunlight was measured using 10 μM aqueous solutions of 2NB. For ice illuminations, solutions were first frozen in a custom-designed, Peltier-cooled, temperature-controlled lab bench freezing chamber (Paige Instruments). Solution or ice samples were then placed in a temperature-controlled chamber with a bottom consisting of an 11 cm × 11 cm copper plate coated with a thin layer of PTFE, and a lid with a 15 cm × 15 cm quartz window to transmit light to the samples. To prevent water condensation at low temperatures, dry air was blown across the top and bottom of the quartz window of the chamber. In our simulated sunlight system (Spectral Energy Corp., model LH 151N) light from a 1000 W Xenon bulb (Osram Sylvania Inc., XBO 1000W/HS OFR) goes through a dichroic cold mirror in the lamp housing (to only transmit wavelengths between 300 and 500 nm) and then a 1.5 G Solar Air Mass filter (Sciencetech Inc., model AM15G) to simulate the total actinic flux at a zenith angle of 48.2°. Sample temperature during illumination was monitored in a blank sample (water or ice) containing a thermocouple.

Before illumination, ice and solution samples were allowed to thermally equilibrate for 30–40 min in the dark. After equilibration, a sample was illuminated for a known amount of time and then either a portion (for aqueous samples) or the entire sample (for ice) was removed. This was repeated for four or five different illumination times for a given sample in order to measure the decay rate constant for 2NB (see below). After illumination, aqueous samples were immediately analyzed for 2NB, while ice samples were first melted in the dark at room temperature (5–10 min). 2NB concentrations were determined using isocratic HPLC with UV detection (Shimadzu SPD-10AV UV/Visible detector (detection $\lambda = 258$ nm); Shimadzu LC10-AT pump; Keystone Scientific C-18 Beta Basic reverse-phase column (250 mm × 3 mm, 3 μm bead) with attached guard column; and TCM 2000 column heater (Analytical Sales and Service Inc.) to maintain the column at 30 °C). The eluent was 60% acetonitrile/40% H_2O, run at a flow rate of 0.60 mL min^{-1}.

To determine the effect of acetonitrile (ACN) on 2NB photochemistry, ACN/H_2O solutions containing 10 μM 2NB were illuminated in 1.0 cm quartz cuvettes with 313 nm radiation from a 1000 W Hg/Xe monochromatic system [6]. Samples were analyzed as described above.

2.4. Calculating the rate constant for 2NB photodecay, j(2NB)

Under low-light-absorbing conditions (such as used in our experiments), 2-nitrobenzaldehyde undergoes first-order photodegradation such that:

$$\ln\left(\frac{[2NB]_t}{[2NB]_0}\right) = -\,j(2NB) \times t \tag{1}$$

where $[2NB]_t$ and $[2NB]_0$ are the concentrations at illumination times t and zero, respectively. Values of the 2NB photodecay rate constant, j(2NB), were determined as the negative of the slope of a plot of $\ln([2NB]_t/[2NB]_0)$ versus t using all time points for a given sample.

Although not used in this study, in solutions containing high concentrations of 2NB (e.g., 0.1 M), the solution absorbs essentially all of the incoming photons and the rate of 2NB photodegradation is zero order [2,9]. Under these conditions the actinometer measures the total photon flux incident upon the sample cell. In contrast, in solutions with low 2NB concentrations, the actinometer is measuring the average photon flux seen by the sample, i.e., the photon flux throughout the entire volume of sample. These two fluxes can be different as a result of light reflection in the sample container or chamber. For example, the effective photon flux in a low-absorbing solution contained in a reflective cell or chamber is higher than the incident photon flux as a result of radiation passing through the solution, reflecting from a surface, and passing back through the solution. This effect is not captured with a high-absorbing solution, since all incident radiation is absorbed. Thus the optical density of 2NB (i.e., either high- or low-absorbing) should be qualitatively matched to the optical density of the illuminated samples. Because most environmental samples have low optical densities, they should be studied in conjunction with low-absorbing 2NB actinometry solutions.

2.5. Illumination of 2NB at Summit, Greenland

The photodegradation of 2NB was also measured on the surface snow at Summit, Greenland (72.6°N, 38.5°W, 3200 m elevation), using 10 μM 2NB solutions both as a liquid in quartz tubes and as ice pellets. Quartz tubes (5 mm ID × 7 mm OD; $L = 58$ or 97 mm) were made from GE 021 tubing (GM Associates, Oakland, CA) and were capped with 5 mm diameter silicone rubber stoppers. Tubes were filled with 2NB solution in the laboratory the morning of each experiment. Ice pellets were made the night before experiments by freezing 0.5 or 1.0 mL of 2NB solution on PTFE sheets in the dark. After freezing, the pellets were kept outdoors (below freezing) in amber glass jars wrapped in aluminum foil. Tubes and pellets were kept in the dark before and after sunlight exposure. Before deploying a tube on the snow, we gently swept away any fresh snow to provide a stable surface, placed a tube onto the snow surface for a measured amount of time, then collected it. This process was rapidly repeated for different illumination times, typically 0–60 s. Ice pellets were similarly exposed except that all pellets were simultaneously scattered onto the snow at time zero, and then pellets were retrieved at known time intervals, and melted individually in the dark after all were retrieved. All samples were analyzed for 2NB by HPLC (Section 2.3) in order to determine j(2NB) values (Section 2.4).

2.6. Calculated j(2NB) values in Greenland

In addition to measuring values of *j*(2NB) on the snow surface, we also calculated values using measured or modeled actinic fluxes:

$$j(2\text{NB}) = 2.303 \times (10^3\ \text{cm}^3\,\text{L}^{-1} \times 1\,\text{mol}/N_\text{A}\,\text{mlc}) \times \Sigma(I'_\lambda \times \Delta\lambda \times \varepsilon_{2\text{NB},\lambda} \times \Phi_{2\text{NB},\lambda}) \quad (2)$$

where N_A is Avogadro's number, I'_λ is the actinic flux (photons cm^{-2} s^{-1} nm^{-1}), $\Delta\lambda$ is the wavelength interval between actinic flux data points (nm), $\varepsilon_{2\text{NB},\lambda}$ and $\Phi_{2\text{NB},\lambda}$ are the base-10 molar absorptivity (M^{-1} cm^{-1}) and quantum yield (molecule photon^{-1}) for 2NB, respectively, and the summation is over all illumination wavelengths λ. Values for I'_λ were either modeled values from TUV (http://www.acd.ucar.edu/Science/Models/TUV/, Tropospheric Ultraviolet and Visible, version 4.0) [18] or measured values at Summit. For the TUV modeled values we used the pseudo-spherical, discrete ordinate, 4-stream model with a wavelength-independent surface albedo of 0.93 [19], ozone column amounts for the day of each experiment at Summit from the ~12:00 UT satellite pass [20], and default values for the other parameters (including a cloud optical depth of 0.0 (i.e., no clouds)). For measured actinic fluxes we used values from the on-site Biospherical Instruments spectroradiometer (SUV-150B) [21].

3. Results and discussion

3.1. Molar absorptivities for 2-nitrobenzaldehyde

As shown in Fig. 1, the molar absorptivity of 2NB has a peak near 260 nm and slowly decreases with increasing wavelength, reaching zero near 430 nm (values over the entire wavelength range, for five temperatures between 25 and 1 °C, are listed in Table S1 of the Supplemental Data). For tropospheric sunlight (i.e., $\lambda > 290$ nm), molar absorptivities decrease only slightly with decreasing temperature between 25 and 1 °C: values of $\varepsilon_{2\text{NB},\lambda}$ at 1 °C are 1–6% lower than values at 25 °C. Our measurements at 25 °C agree very well with those previously reported (Table 1), as shown by the open circles in Fig. 1. The relative percent differences between our data (Table S1) and these previously reported values at 313, 334, 366, and 405 nm (Table 1) are 0.8%, 0.6%, 1.3%, and 7.3%, respectively.

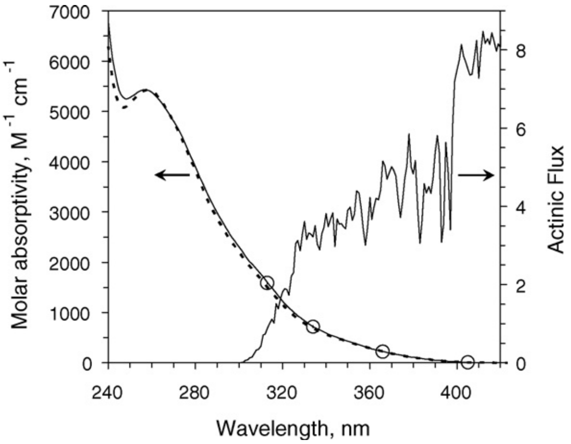

Fig. 1. Base-10 molar absorptivities of 2-nitrobenzaldehyde in water at 1 °C (dashed line) and 25 °C (solid line) along with previously reported values (open circles) [7,8,22]; error bars for each previously reported value are smaller than the symbols. Actinic fluxes (solid line; right axis; units of 10^{14} photons cm^{-2} s^{-1} nm^{-1}) are measured values at ground level at Summit, Greenland during summer (midday) from Biospherical Instruments [21].

Table 1
2-Nitrobenzaldehyde molar absorptivities and quantum yields in solution and in solid phases, listed in chronological order from oldest to most recent.

λ (nm)	T (°C)	$\varepsilon_{2\text{NB},\lambda}$[a] (M^{-1} cm^{-1})[b]	$\Phi_{2\text{NB},\lambda}$ (mol mol^{-1})[b]	Solvent	Ref.
Solution values					
"Violet light"	RT[c]		0.5	"Aldehyde"	[23]
366	22–24	181	0.52	Ligroin	[24]
366	22–24	184	0.51	Acetone	[24]
404	22–24	35.6	0.46	Acetone	[24]
350	RT[d]		0.41 ± 0.06	Benzene (dry)	[29]
350	RT[d]		0.44 ± 0.06	Benzene (moist)	[29]
350	RT[d]		0.50 ± 0.06	Acetonitrile	[29]
350	RT[d]		0.39 ± 0.06	Methanol	[29]
313	20	1590 ± 19	0.40 ± 0.03	Water	[7]
334	20	720 ± 17	0.42 ± 0.02	Water	[7]
366	20 ± 1	224 ± 2	0.42 ± 0.02	Water	[22]
405	RT[d]	11.9 ± 0.5	0.39 ± 0.04	Water	[8]
280–380	RT[d]		0.41 ± 0.02	Water	[3]
313	20	933 ± 11	0.43 ± 0.03	Acetonitrile	This study
Recommended value					
280–405	1–28		0.41 ± 0.02	Water or organic	This study
Solid phase values					
390–440	RT[d]		0.44 ± 0.06	2NB crystals	[23]
395–435	RT[d]		0.58 ± 0.15	2NB crystals	[23]
265	22–24		0.4–0.5	2NB crystals	[24]
313	22–24		0.51	2NB crystals	[24]
366	22–24		0.50	2NB crystals	[24]
313 ± 20	−25	976		Water ice	[10]
Recommended value					
280–405	−25 to 0		0.41 ± 0.04	Water ice	This study

[a] Base-10 molar absorptivity.
[b] Listed uncertainties are ±1σ.
[c] Assumed to be room temperature.
[d] Room temperature.

3.2. Review of 2NB quantum yield data in solution and recommended value

From 1924 to the present there have been numerous measurements of the quantum yield for 2-nitrobenzaldehyde (Φ_{2NB}) in water and organic solvents. The early data indicated that Φ_{2NB} is approximately 0.5 [23,24], and this value is frequently cited as the solution value [1,2,15,16]. However, a compilation of the available solution data shows three important points (Table 1): (1) the quantum yield for 2NB in water is closer to 0.4, (2) this value is independent of wavelength between approximately 280–400 nm [3,7,8,22], which allows 2NB to be used as a polychromatic quantum counter [1], and (3) the quantum yield also appears to be 0.4 in other solvents. The average ($\pm\sigma$) value of Φ_{2NB} in water from the single-wavelength studies by Anastasio, Arakaki, and co-workers (at 313, 334, 366, and 405 nm; Refs. [7,8,22] in Table 1) is 0.41 ± 0.02, which is the same as the value obtained under polychromatic illumination (280–400 nm) in water by Phillips and Simpson (Ref. [3]; Table 1). Similarly, quantum yields determined in benzene, acetonitrile, and methanol (Table 1) are all consistent with a value of 0.41. Thus we recommend a value for Φ_{2NB} of 0.41 ± 0.02 for liquid studies with water and organic solvents.

What are the implications of this value compared to the typically quoted value of 0.50? They are significant for studies that use 2NB actinometry to determine photon fluxes during monochromatic or sunlight illuminations. With monochromatic illumination and low-absorbing solutions, the photon flux (I_λ, mol-photons L^{-1} s^{-1}) is calculated using:

$$I_\lambda = \frac{j(2NB)}{2.303 \times \varepsilon_{2NB,\lambda} \times \Phi_{2NB,\lambda} \times l} \qquad (3)$$

where $\varepsilon_{2NB,\lambda}$ and $\Phi_{2NB,\lambda}$ are as described above and l is the cell path length (cm). Thus using a value of Φ_{2NB} of 0.50 (instead of 0.41) leads to an 18% underestimate of the photon flux in the sample. In experiments where this photon flux is used to determine quantum yields for a given photochemical process i (e.g., $\Phi(NO_3^- \rightarrow NO_2^-)$), the resulting value of Φ_i will be overestimated by 18% because of the error in Φ_{2NB}. A similar error will be present in studies that use j(2NB) (with Φ_{2NB} of 0.50) to estimate photon fluxes from polychromatic radiation sources such as solar simulators. In contrast, in studies where j(2NB) is used to scale the rate of a photochemical process from laboratory simulated sunlight to actual sunlight conditions, the results are independent of the 2NB quantum yield and thus will be unaffected by this error.

Finally, while the works of Bowen et al. [23] and Leighton and Lucy [24] have been cited as showing that the quantum yield for 2NB in the gas phase is also 0.50 [2,16], these early papers do not describe any gas-phase experiments. As far as we can determine, the first gas-phase study of 2-nitrobenzaldehyde photochemistry was only recently published by Zhu and co-workers, whose results suggest that the quantum yield for photodegradation of gaseous 2NB at 25 °C ranges from unity at 290–310 nm to zero at 350 nm [25].

3.3. Temperature and phase dependence of Φ_{2NB}

One point that has been unanswered by the past reports in Table 1 is how Φ_{2NB} in water depends on temperature. To investigate this issue, we illuminated dilute 2NB solutions with simulated sunlight between −23 °C and +28 °C. As shown in Fig. 2, on any given experimental day j(2NB) in water is essentially invariant with temperature: the slope of the linear regression fit to the solution data is statistically no different from zero on each individual experiment day. As illustrated by Eq. (2), under sunlight illumination (whether real or simulated) the rate constant for 2NB decay is proportional to the product of the photon flux, quantum yield, and molar absorptivity for 2NB, summed over all wavelengths. Since the photon flux is constant on a given day in our experiments, and the molar absorptivity for 2NB varies by only 1–6% across the range of temperatures examined (Fig. 1 and Table S1), the fact that j(2NB) in solution is constant across temperature (Fig. 2) indicates that the quantum yield for 2NB is essentially independent of temperature.

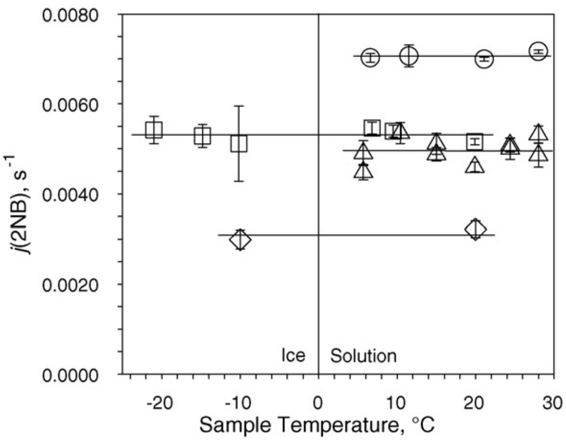

Fig. 2. Temperature- and phase-dependence of 2NB photolysis rate constants during illumination in the laboratory with simulated sunlight. Each symbol type represents results from a single day of experiments, with the horizontal line representing the average value for j(2NB) on that day: circles represent solutions in 4-mL quartz cuvettes; squares and triangles are for samples held in 1-mL PTFE Teflon beakers; diamonds are for samples held in 1-mL stoppered quartz tubes. Error bars represent ±1 standard error, calculated from the SE of the regression slope (Eq. (1)).

To investigate whether j(2NB) is different in water ice compared to in liquid water, on two of our experimental days we measured 2NB decay in both solution and ice (alternating between in the two phases for subsequent experiments throughout each day). We found there is no significant difference in j(2NB) between solution and ice on a given day. Because the ice samples are transparent, and because the same containers were used for both solution and ice samples, we expect that the photon flux is essentially the same in these two different types of samples. Thus the fact that j(2NB) is the same in water and ice indicates that Φ_{2NB} is also the same in these two phases. This result is consistent with some of the earliest studies of 2NB photolysis (Table 1), where the quantum yield for 2NB photolysis in solid samples was found to be essentially the same as in solution [23,24]. Given this, our recommended value for Φ_{2NB} in water ice (as well as for other solid phases) is the same as in solution: 0.41 ± 0.04 (Table 1), with the error (1σ) estimated based on the ratio of the relative standard deviations of ice and solution j(2NB) values in our experiments. Interestingly, most of the results from the solid-phase studies of Bowen et al. [23] are more consistent with a quantum yield of 0.41 than they are with the frequently cited value of 0.50 that is ascribed to these authors (Table 1).

The fact that the quantum yield of 2-nitrobenzaldehyde is independent of temperature, solvent, and phase makes this species a versatile, robust, and simple actinometer. This is in contrast to a number of other actinometers that have been used for solution and solid-phase studies, such as valerophenone, whose photochemistry depends upon temperature, phase, and solvent [26].

3.4. Action spectrum for 2NB photolysis

To examine the relative importance of different solar wavelengths for 2NB photochemistry in the environment, we calculated the action spectrum for 2NB photolysis using Eq. (2) with the measured summer, midday, actinic flux at Summit, Greenland. As shown in Fig. 3, the peak in 2NB reactivity is between 320 and 340 nm, while wavelengths from approximately 300–400 nm con-

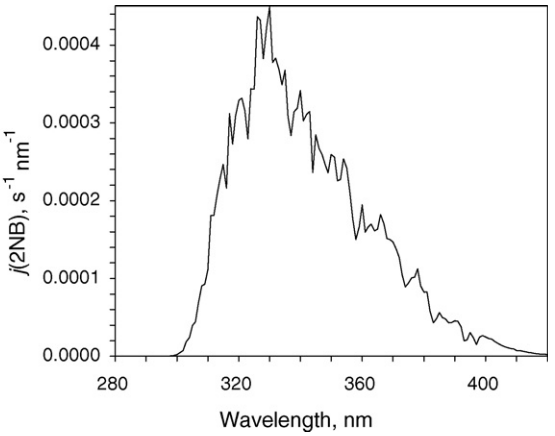

Fig. 3. Action spectrum for 2NB photolysis based on molar absorptivity values at 1 °C and the spectral actinic flux at Summit, Greenland at midday during summer (ground level, clear sky) [21].

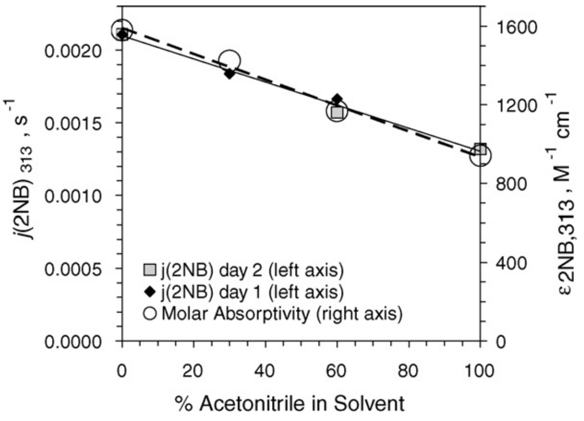

Fig. 4. Effect of acetonitrile on the photochemistry of 2-nitrobenzaldehyde. The open circles (and dotted line) represent the 2NB molar absorptivities at 313 nm ($\varepsilon_{2NB,313}$), while the squares and diamonds (and solid line) are rate constants for 2-nitrobenzaldehyde photolysis during 313 nm illumination ($j(2NB)_{313}$) on two different days. To adjust for the small difference in the lamp output between the two days, values of j(2NB) on the second day (gray squares) are scaled so that the value in 0% acetonitrile (i.e., water) is the same as on the first test day. The lines are regression fits: $\varepsilon_{2NB,313}$ ($M^{-1}\,cm^{-1}$) = 1590–6.57 (% acetonitrile) and $j(2NB)_{313}$ = 0.00210–7.94 × 10^{-6} (% acetonitrile).

tribute to the photochemistry. Because the quantum yield for 2NB is independent of temperature (Section 3.3), and the 2NB molar absorptivities are only weakly dependent upon temperature (Section 3.1), the action spectrum for 2NB is only weakly dependent upon temperature. For example, the area under the action spectrum curve in Fig. 3 (calculated for a temperature of 1 °C) would increase by only 3% at a temperature of 25 °C.

A number of important snowgrain chromophores have action spectra that peak in the same range as 2NB, such as NO_2^-, NO_3^-, and HOOH, which have action spectra centered around 346, 318, and 324 nm, respectively [12]. Thus 2NB could be used as a field actinometer to scale rate constants for the photolysis of NO_2^-, NO_3^-, or HOOH as a function of solar zenith angle.

3.5. Effect of acetonitrile on 2NB photochemistry

To examine whether the presence of acetonitrile affects 2NB photolysis, we illuminated dilute solutions of 2NB in acetonitrile–water mixtures using 313 nm radiation. As shown in Fig. 4, j(2NB) decreases linearly with increasing acetonitrile in solution: moving from 100% water as solvent to 100% acetonitrile reduces j(2NB) by 38%. This decrease in j(2NB) is mirrored by a very similar decrease in the molar absorptivity of 2NB: $\varepsilon_{2NB,313}$ in acetonitrile is 41% lower than the value in water. Based on the regression data in Fig. 4, and using our recommended value for Φ_{2NB} in water, we calculate that Φ_{2NB} (±1σ) in acetonitrile is 0.43 ± 0.03, which is not statistically significantly different from the water value (0.41 ± 0.02; Table 1). Our 2NB quantum yield in acetonitrile is also not statistically different from that of George and Scaiano (Table 1), although their value is 16% higher than ours.

3.6. Use of 2NB as a low temperature actinometer in the field

To test whether 2-nitrobenzaldehyde is a useful actinometer for snow photochemistry studies, we performed a number of tests on the surface snow at Summit, Greenland during the summer of 2005 (Table 2). As described in Section 2.5, tests were performed both using water solutions (not frozen) in quartz tubes, as well as frozen water-ice pellets, which were put on the surface snow and monitored for 2NB photodegradation. Examples of 2NB decay plots during illumination are shown in Fig. 5, in this case for three different times of day during the diurnal test on August 6. The full set of measurements made during this day is shown in Fig. 6. These data show the expected diurnal pattern for j(2NB) and illustrate that 2NB is useful over a wide range of actinic fluxes, from very low (e.g., the measurements made at 23:00 local time) to quite high (e.g., near midday).

Table 2
Quartz tube, ice pellet and TUV-derived values for j(2NB) at Summit, Greenland.

Date[a]	Local time	Solvent	Measured j(2NB), s^{-1}	RSE[b]	Measured j(2NB)/ TUV j(2NB)[c]	Weather
Actinometry solutions in quartz tubes						
June 29	10:02	Water	0.025	0.04	1.33	Very cloudy, light wind (3–4 kts)
July 30	12:24	Water	0.022	0.02	1.22	Windy (13 kts), snowy, and overcast
July 30	15:51	Water	0.017	0.01	1.16	Windy (10 kts), snowy, and overcast
July 30	20:18	Water	0.005	0.02	1.28	No wind and clearing up
August 6	06:00–23:00[d]	Water	0.00043–0.030	0.02[e]	1.56 ± 0.13[f]	Very clear, very sunny, no wind, T = −23 to −5 °C
Actinometry ice pellets						
June 19	18:38–19:04	Water ice	0.008	0.12	0.78	Very clear, very sunny
June 29	10:19	Water ice	0.018	0.07	0.94	Very cloudy, light wind (3–4 kts)
June 29	10:23	Water ice	0.019	0.15	0.97	Very cloudy, light wind (3–4 kts)

[a] Experiments were conducted at Summit, Greenland during the summer of 2005.
[b] Relative standard error (RSE) = SE (j(2NB))/j(2NB).
[c] Measured j(2NB) divided by calculated j(2NB) based on modeled TUV actinic fluxes for clear-sky conditions.
[d] Diurnal test, see Fig. 6.
[e] Average RSE of 16 measurements made throughout the day.
[f] Listed value is mean ± 1σ.

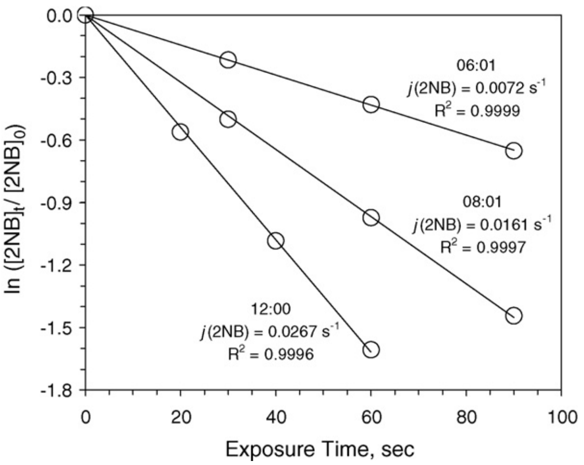

Fig. 5. Decay plots of 2NB measured on surface snow at Summit, Greenland on August 6, 2005 at 06:01, 08:01, and 12:00 local time using aqueous solutions in quartz tubes. Open circles represent measured data points; solid lines are fitted regression lines.

However, the measured *j*(2NB) values in Fig. 6 are significantly higher than those calculated based on either modeled (TUV) or measured (Biospherical) near-surface actinic fluxes. The good agreement between the two sets of calculated *j*(2NB) values shows that the modeled and measured actinic fluxes are very close. However, on average, the measured *j*(2NB) value is 56% higher than the *j*(2NB) value calculated using measured (or modeled) actinic flux (Table 2), with no clear trend in this ratio throughout the day. In the other field tests with 2NB solutions in quartz tubes, the measured value of *j*(2NB) was also greater than the calculated value based on the TUV actinic flux. The discrepancy is smaller in these tests (measured/calculated ratios of *j*(2NB) range from 1.16 to 1.33; Table 2), but this is not a sign of improved performance. Rather, these days were cloudy, which decreased the measured *j*(2NB), but was not accounted for in the TUV modeled actinic flux, which assumed clear skies. In contrast to these quartz tube experiments, the results from the ice pellet experiments better match the rate constants calculated from modeled actinic fluxes (e.g., the solution and ice results on June 29), although the ice pellet tests were quite noisy (as shown by the high relative standard errors; Table 2).

Why are values of *j*(2NB) faster than predicted for the solution experiments in quartz tubes? It does not appear to be associated with the tubes themselves: in our previous work we examined the photolysis of hydrogen peroxide and nitrate at Summit, using aqueous acetonitrile solutions in quartz tubes [27,28]. Unlike our current 2NB work, there was no evidence for an actinic flux enhancement in HOOH or NO_3^- photolysis: on average ($\pm 1\sigma$), the ratios of the measured rate constants in quartz tubes to the calculated values based on measured actinic fluxes were 1.3 ± 0.3 for HOOH and 1.1 ± 0.6 for NO_3^-. One difference between this past work (HOOH and NO_3^-) and the current work (2NB) is that the HOOH and NO_3^- tubes (containing acetonitrile and water) were precooled to the ambient freezing temperature prior to deploying on the snow, while the 2NB tubes (containing water) were kept at room temperature until deploying. Based this, we hypothesize that the room temperature 2NB tubes melted some of the surface snow and sank a small amount into the snow; this would increase reflection from the snow surface and increase the actinic flux inside the tubes, which would enhance 2NB photodegradation. We did not cool the 2NB tubes in order to prevent the solutions from freezing and breaking the tubes. Solving this issue (e.g., by using sturdier tubes and allowing the solutions to freeze before use, or by using water/acetonitrile as a solvent to prevent freezing) should allow 2NB to be used as a relatively simple field actinometer.

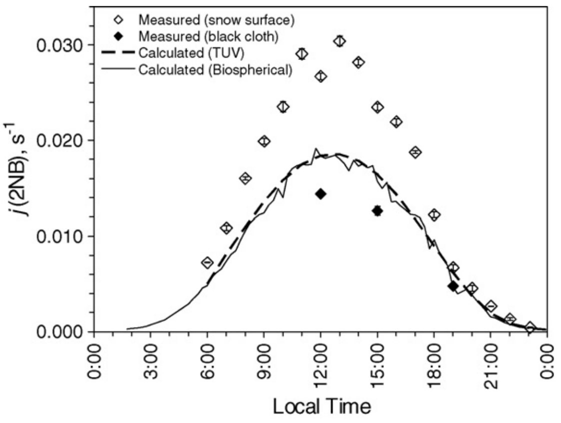

Fig. 6. Diurnal variation in *j*(2NB) measured on the snow surface on August 6, 2005 at Summit using aqueous solutions in quartz tubes (open diamonds). Black diamonds represent results measured in tubes put on a black cloth on the surface to prevent reflection from the snow surface. Error bars represent 1 standard error. The solid and dashed lines are *j*(2NB) values calculated using modeled (TUV; Ref. [18]) and measured (Biospherical; Ref. [21]) actinic fluxes, respectively, at Summit on this day.

4. Conclusions

Our experiments show that the quantum yield for 2-nitrobenzaldehyde photolysis in solution is independent of temperature and is the same in solid water ice as in liquid water. Based on a review of the literature, we recommend a wavelength-independent value of 0.41 for both liquid and solid phases, which is 18% lower than the value of 0.50 that is typically used; as described in Section 3.2, this difference has important implications for studies that use 2NB to determine photon fluxes. In addition, the 2NB quantum yield is the same in water and organic solvents, although solvent does affect the molar absorptivities of 2NB.

2NB is a convenient, robust chemical actinometer, with fast time resolution and straightforward photochemistry. While our field results for 2-nitrobenzaldehyde photodecay in the Greenland snowpack generally were higher than calculated based on measured or modeled actinic fluxes, this problem appears to be readily correctable for future studies. In addition, while we measured 2NB decay via HPLC, it is also possible to monitor this reaction with either UV–vis absorption spectrophotometry [3] or, in solutions with high optical densities, by using changes in pH (since the product of the 2NB photoreaction, 2-nitrosobenzoic acid, releases a proton into solution) [2,9].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2009.11.013.

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