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Temperature dependence of the UV absorption cross sections and photodissociation products of C_3-C_5 alkyl nitrates

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Abstract

Cavity ring-down spectroscopy has been used to measure the UV absorption cross sections of 1-propyl, 2-propyl, 1-butyl, and 1-pentyl nitrates as a function of temperature between 265 and 340 nm. Absorption cross sections increased with temperature from 238 to 298 K. The photodissociation of these C_3-C_5 alkyl nitrates at 308 nm was investigated; the exclusive fragmentation channel was cleavage of the RO-NO₂ bond to form RO + NO₂. The NO₂ yield was 1.0 ± 0.1, with no temperature dependence. Tropospheric photolysis rates of C_3-C_5 alkyl nitrates were calculated. © 1997 Elsevier Science B.V.

1. Introduction

Alkyl nitrates (RONO₂), formed in the atmosphere primarily by reactions [1] of alkyl peroxy radicals (RO₂) with NO, play important roles in atmospheric chemistry[2]. Although alkyl nitrates are a relatively small fraction of the total reactive odd nitrogen (NO_Y) in processed air masses [3,4], they represent a very significant fraction of NO_Y in Arctic winter night air masses [5,6] and are long enough lived to be transported over long distances. Therefore, a detailed understanding of their atmospheric removal processes is necessary.

Alkyl nitrates exhibit a strong $\pi \rightarrow \pi^*$ absorp-

tion band centered around 190 nm and a weaker $n \rightarrow \pi^*$ absorption band with a maximum at ~ 260 nm [7,8]. Because their reactions with OH radicals are insignificant compared with photolytic loss [9-12] and because they are not significantly removed by wet deposition [13], photolysis of alkyl nitrates at near-UV wavelengths is an important destruction process in the troposphere [14,15]. Photolysis rates of ethyl, 1-propyl, 1-butyl, and 2-butyl nitrates were found to be strongly temperature dependent between 279 and 299 K, with an effective activation energy of 11.2 kJ mol⁻¹ for 2-butyl nitrate and 10.1 kJ mol⁻¹ for ethyl nitrate [14,16]. This temperature dependence was attributed to an increase in absorption cross section due to the significant contribution from a higher vibrational level at room temperature. Although temperature-dependent cross section data have

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been reported for methyl, ethyl, and 2-propyl (*i*- $C_3H_7ONO_2$) nitrates [17–21], such information is not available for larger alkyl nitrates such as 1-propyl nitrate (*n*- $C_3H_7ONO_2$), 1-butyl nitrate (*n*- $C_4H_9ONO_2$), and 1-pentyl nitrate (*n*- $C_5H_{11}ONO_2$). Absorption cross sections of C_3-C_5 alkyl nitrates as a function of temperature will allow atmospheric photolysis rate calculation and an examination of the dependence of absorption cross sections and their temperature coefficients on alkyl chain length.

Photodissociation of C_3-C_5 alkyl nitrates can occur through the following channels:

$$RONO_2 + h\nu \rightarrow RO + NO_2 \quad (\Delta^{\circ}H_{298})$$
$$= 166 \text{ kJ/mol}; \ \lambda_{\text{threshold}} = 720 \text{ nm}), \qquad (1a)$$

 $\begin{aligned} \text{RONO}_2 + h\nu &\to \text{R} + \text{NO}_3 \quad (\Delta^\circ H_{298} \\ &= 339 \text{ kJ/mol}; \ \lambda_{\text{threshold}} = 352 \text{ nm}), \end{aligned} \tag{1b}$

$$RONO_2 + h\nu \rightarrow R'CHO + HONO \quad (\Delta^{\circ}H_{298}$$
$$= -93 \text{ kJ/mol}), \qquad (1c)$$

$$RONO_2 + h\nu \rightarrow RONO + O(^{3}P) \quad (\Delta^{\circ}H_{298})$$
$$= 295 \text{ kJ/mol}; \ \lambda_{\text{threshold}} = 405 \text{ nm}), \qquad (1d)$$

where these enthalpy changes for 1-propyl nitrate are taken to be representative of those for C_3-C_5 alkyl nitrates, and photochemical thresholds are calculated from the corresponding enthalpy changes. Pathways (1a) and (1b) are energetically accessible at a photodissociation wavelength of 308 nm. Although the calculated thermochemical threshold for pathway (1a) is 720 nm, its photochemical threshold is in the near-UV region due to the lack of an allowed electronic transition [8]. Channel (1c) is exothermic, but hindered by a dissociation energy barrier. Channel (1d) is energetically allowed but spin forbidden, and is not expected to be a major process. The significant photodissociation pathways at 308 nm are thus expected to be (1a) and (1b). One previous study [22] reported observation of NO₂ following 193 nm photolysis of 1-propyl nitrate, but the NO₂ product yield was not measured. This Letter presents temperaturedependent UV absorption cross section data for 1propyl, 2-propyl, 1-butyl, and 1-pentyl nitrates, which were measured by using a sensitive new detection technique, cavity ring-down spectroscopy [23,24]. In addition, product channels and quantum yields from

308 nm excimer laser photodissociation of these C_3-C_5 alkyl nitrates have been determined.

2. Experimental

The experimental apparatus has been described in detail elsewhere [19,25,26]. The output from an excimer laser (0.026-0.045 J/cm²) entered the reaction cell at a 15° angle with the main cell axis through a side arm and overlapped the probe beam at the center of the cavity. The probe laser pulse was directed along the main optical axis of the cell vacuum-sealed with a pair of high-reflectance cavity mirrors. A fraction of the probe laser output was transmitted into the cavity through the front mirror. The photon intensity decay inside the cavity was measured from the weak transmission of light through the rear mirror with a photomultiplier tube (PMT). The PMT output was amplified, digitized, sent to a computer, and the total loss per optical pass was calculated. Absorption cross section was acquired by determining optical loss due to sample absorption as a function of its pressure in the cell. Absorption spectra were recorded by scanning the wavelength of the probe laser with a digital drive unit.

A jacketed copper cell was used in temperaturedependent cross section measurements. The cell temperature was controlled by circulating cooled ethanol through its outer jacket using a low-temperature bath/circulator and was constant to within $\pm 1 \text{ K}$ over the entire length. The temperature dependence of photolysis was examined by varying the temperature inside the reaction chamber with a cooled stainless-steel coil coaxial with the main optical axis of chamber. The temperature the in the photolysis/probe laser overlapping region was constant to within ± 2 K.

 C_3-C_5 alkyl nitrates were obtained from the following suppliers: 1-propyl nitrate ($\geq 97\%$; Fisher Scientific), 2-propyl nitrate ($\geq 99\%$; Aldrich), 1butyl nitrate ($\geq 95\%$; Eastern Chemical), and 1pentyl nitrate ($\geq 99\%$; TCI America). Alkyl nitrate samples were purified by repeated vacuum distillations. Typical alkyl nitrate pressures used in the cross section measurements varied between 0.01 and 10 Torr, while photolysis studies were carried out with alkyl nitrate pressure ranging between 1 and 10 Torr.

3. Results and discussion

3.1. UV absorption cross sections at 298 K

3.1.1. Absorption cross sections of 1- and 2-propyl nitrates

Illustrated in Fig. 1 are the room temperature UV absorption spectra of 1- and 2-propyl nitrates recorded in the wavelength range 265-340 nm by using cavity ring-down spectroscopy. The UV spectra of 1- and 2-propyl nitrates are similar in shape, but the cross sections of 2-propyl nitrate are significantly larger. Relative uncertainty for cross section measurements is ~ 5%, which includes the standard deviation for each measurement (< 1%) plus standard deviations about the mean of several measurements. Roberts and Fajer [27], Turberg et al. [28], and Clemitshaw et al. [20] reported room-temperature absorption cross sections of 1-propyl nitrate;

their results have been included in Fig. 1 for comparison. As seen from this figure, our cross section results are in reasonable accord with those obtained by Roberts and Fajer over the entire wavelength range examined. Although cross section data reported by Turberg et al. agree with our values in the range 265–315 nm, their results are significantly higher at longer wavelengths. Cross section values reported by Clemitshaw et al. also diverge at longer wavelengths. For 2-propyl nitrate, there is good agreement between our cross section data and those obtained by Roberts and Fajer [27], Talukdar et al. [21], and Clemitshaw et al. [20] Cross section values reported by Turberg et al. [28] diverge at longer wavelengths.

3.1.2. Dependence of absorption cross section on alkyl chain length

Absorption spectra of 1-butyl and 1-pentyl nitrates have been measured at 298 K; they are similar in shape to those of 1-propyl and 2-propyl nitrates. Listed in Table 1 are absorption cross sections of 1-propyl, 1-butyl, and 1-pentyl nitrates determined in



Fig. 1. Absorption cross sections of 1- and 2-propyl (×10) nitrates in the 265–340 nm region: this work at 298 K (solid line); this work at 258 K (dotted line). Previous determinations of 1-propyl nitrate cross sections at 298 K: Turberg et al. [28] (\bigcirc), Roberts and Fajer [27] (\diamondsuit), and Clemitshaw et al. [20] (\Box). Previous determinations of 2-propyl nitrate cross sections at 298 K: Turberg et al. [28] (\circ), Roberts and Fajer [27] (\diamondsuit), Talukdar et al. [21] (∇), and Clemitshaw et al. [20] (\blacksquare).

Table 1	
Absorption cross sections (298 K) and absorption cross section temperature coefficients of C_2-C_5 alkyl nitra	ates

λ(nm)	C ₂ H ₅ ONO ₂		n-C ₃ H ₇ ONO ₂		<i>i</i> -C ₃ H ₇ ONO ₂		<i>n</i> -C ₄ H ₉ ONO ₂		$n-C_5H_{11}ONO_2$	
	$\sigma \times 10^{20}$	$B \times 10_3$	$\overline{\sigma \times 10}^{20}$	$B \times 10^3$	$\sigma \times 10^{20}$	$B \times 10^3$	$\sigma \times 10^{20}$	$B \times 10^3$	$\overline{\sigma \times 10^{20}}$	$B \times 10^3$
265	3.57	3.40	3.82	3.29	4.56	3.27	3.87	3.67	4.09	3.34
270	3.19	3.62	3.30	3.44	4.09	3.39	3.49	3.76	3.72	3.65
275	2.61	3.74	2.79	3.72	3.42	3.91	3.27	3.80	3.00	3.93
280	2.15	3.87	2.47	3.98	2.70	3.85	2.66	4.29	2.70	4.12
285	1.67	4.08	1.87	4.22	2.22	4.25	2.04	4.33	2.03	4.25
290	1.21	4.39	1.44	4.76	1.57	4.73	1.48	4.59	1.50	4.69
295	0.855	4.86	0.964	4.94	1.21	4.92	1.03	4.70	0.969	4.96
300	0.568	5.33	0.643	5.11	0.874	5.08	0.716	5.27	0.710	5.42
305	0.353	5.73	0.411	5.66	0.552	5.38	0.467	5.57	0.453	5.61
310	0.196	6.05	0.236	6.41	0.350	6.16	0.271	6.02	0.277	6.07
315	0.119	7.01	0.136	6.79	0.201	6.95	0.154	7.06	0.151	6.98
320	0.0628	7.78	0.0685	7.89	0.105	7.61	0.0759	7.87	0.0785	7.71
325	0.0285	8.77	0.0319	8.90	0.0524	8.80	0.0350	9.15	0.0367	8.80
330	0.0127	10.2	0.0139	9.66	0.0230	9.93	0.0165	10.3	0.0177	9.75
335	0.00552	11.7	0.00634	11.5	0.0106	11.5	0.00817	11.9	0.00843	11.5
340	0.00248	13.8	0.00286	14.5	0.00494	13.8	0.00353	15.1	0.00392	14.9

the present work along with our previous results [19] from ethyl nitrate. The absorption cross sections show a slight increase with increasing carbon chain length for $\leq C_4$ alkyl nitrates, and are approximately the same for 1-butyl and 1-pentyl nitrates. The observed dependence of absorption cross section on alkyl chain length can be explained in terms of the electronic effect that alkyl substitution has on the $-ONO_2$ chromophore. Since alkyl substituents are electron donors, their contribution to the electron density on the $-ONO_2$ group is expected to increase with alkyl chain length initially, and then level off at longer chain length, as observed experimentally.

3.2. Absorption cross section temperature dependence

3.2.1. Temperature dependence of the absorption cross sections of 1- and 2-propyl nitrates

The UV absorption spectra of 1- and 2-propyl nitrates were acquired at 238, 248, 258, 268, 278, 288, and 298 K. Fig. 1 compares absorption cross sections of 1- and 2-propyl nitrates in the 265–340 nm region at 258 and 298 K. It can be seen that the absorption cross sections show a pronounced increase at higher temperatures throughout the wavelength range studied. The relative uncertainty for cross section measurements is < 10% for $T \ge 258$ K,

and is $\sim 20\%$ in the 334–340 nm region at 238 and 248 K owing to the limited vapor pressure at these low temperatures in combination with small absorptions at longer wavelengths. The temperature-dependent cross section data fit the following equation:

$$\ln \sigma_T - \ln \sigma_{298} = B(\lambda)(T-298)$$
,

where σ_T is the absorption cross section at temperature *T* and $B(\lambda)$ is the absorption cross section temperature coefficient. Illustrated in Fig. 2 are $B(\lambda)$ values for 1- and 2-propyl nitrates obtained from the slope of a linear least-squares analysis of ln σ_T as a function of *T*. $B(\lambda)$ values for 1- and 2-propyl nitrates are similar in magnitude and exhibit a distinct increase at longer wavelengths. Also included in Fig. 2 are $B(\lambda)$ values for 2-propyl nitrate reported by Talukdar et al. [21]. There is good agreement between our results and theirs at wavelengths shorter than 310 nm. The difference increases at longer wavelengths, but still within experimental uncertainty of both studies.

3.2.2. Dependence of absorption cross section temperature coefficient on alkyl chain length

Absorption cross sections of 1-butyl and 1-pentyl nitrates have been measured as a function of temperature in the range 238–298 K, and show a distinct increase with increasing temperature. Listed in Table



Fig. 2. Absorption cross section temperature coefficient (B) as a function of wavelength. 1-propyl nitrate: this work (solid line); 2-propyl nitrate: this work (dotted line), Talukdar et al. [21] (solid circle).

1 are absorption cross section temperature coefficients determined for 1-propyl, 2-propyl, 1-butyl, and 1-pentyl nitrates, along with our earlier results [19] for ethyl nitrate. As seen from Table 1, there is no obvious dependence of $B(\lambda)$ on alkyl chain length, probably because the -ONO₂ chromophore is responsible for near-UV absorption in all these alkyl nitrate molecules. Although Luke and Dickerson [14] reported a factor-of-2 difference in the measured alkyl nitrate photolysis rates between 279 and 299 K, later measurements by Luke et al. [16] indicated a difference of $\sim 33\%$, which is in better agreement with the photolysis rate difference of \sim 17% calculated using our wavelength- and temperature-dependent cross sections. Luke et al.'s study only gave wavelength-integrated photolysis rates as a function of zenith angle within a very limited temperature range and their results depended upon the ambient light conditions unique to the measurement site and time. The wavelength- and temperature-dependent cross section data obtained from the present study allow us to calculate alkyl nitrate photolysis rates as a function of zenith angle, temperature, altitude, and other atmospheric conditions.

3.3. Photodissociation product channels and quantum yields at 308 nm

3.3.1. Photolysis product channels and quantum yields of 1- and 2-propyl nitrates

The cavity ring-down spectrometer was tuned to several near-UV and visible regions to search for absorption from likely photodissociation products of 1- and 2-propyl nitrates. Fig. 3 is a lossmeter absorption spectrum in the 438-452 nm range of the product obtained following 308 nm photolysis of 2-propyl nitrate. The similarity of the photoproduct lossmeter spectrum to that of NO2 indicates that NO_2 is a photolysis product. To determine whether HONO and *i*-C₃H₇ONO are photodissociation products, the product absorption spectrum in the wavelength region 360-374 nm was compared with those of HONO and i-C₃H₇ONO; HONO and i- C_3H_7 ONO were not detected. The cavity ring-down spectrometer was also tuned to the NO₃ absorption band in the 620-670 nm region; the NO₃ radical was not observed. The dominance of the 2-propyl nitrate photodissociation channel yielding $i-C_3H_7O + NO_2$ at 308 nm can be explained in terms of its being a



Fig. 3. Loss meter absorption spectra in the range 438-452 nm: upper trace, 2-propyl nitrate photolysis product; lower trace, NO₂.

pathway involving simple scission of the weakest bond in *i*-C₃H₇ONO₂ ($D_0 = 171$ kJ/mol). Formation of *i*-C₃H₇ + NO₃ is energetically allowed but does not occur. A selective photofragmentation mechanism with electronic excitation localized on the NO₂ moiety during dissociation could explain the absence of the NO₃ product channel. A transfer of energy from the excited NO₂ group to the *i*-C₃H₇O group would be required in order to form *i*-C₃H₇ + NO₃. The exclusive photolysis pathway for 1-propyl nitrate at 308 nm is the production of *n*-C₃H₇O + NO₂.

The yield of NO_2 following photodissociation of $n-C_3H_7ONO_2$ and $i-C_3H_7ONO_2$ at 308 nm was derived from the number of NO_2 molecules formed in the photolysis/probe laser overlapping region per 308 nm photon absorbed by 1- or 2-propyl nitrate. The number of absorbed 308 nm photons was computed from the difference in the photolysis photon intensities at the beginning and at the end of the overlapping region. The incident light intensity was monitored with a Joulemeter calibrated by using

acetone photolysis actinometry [29]. The NO₂ photoproduct concentration was obtained from lossmeter measurements of its absorption at 446.1 nm. The yield of NO₂ was 1.0 ± 0.1 for both 1- and 2-propyl nitrates, independent of propyl nitrate pressure and total pressure. The total pressure was varied between 4 and 760 Torr using N₂ as the buffer gas. The NO₂ product yield was also measured at 278, 283, 288, and 293 K, and was found to be independent of temperature.

3.3.2. Dependence of photolysis pathways and quantum yields on alkyl chain length

The pathways and quantum yields following 308 nm photolysis of 1-butyl and 1-pentyl nitrates have been determined. $RO + NO_2$ was found to be the sole photodissociation pathway, with a quantum yield of 1.0 ± 0.1 . The lack of dependence of photofragmentation product channels and quantum yields on alkyl chain length supports a selective fragmentation mechanism with little transfer of electronic excitation from the NO₂ group to the RO group during dissociation. Similarity in the photolysis quantum yields for C_3-C_5 alkyl nitrates is also consistent with similarity in their absorption spectra and predissociation (non-RRKM dissociation) of alkyl nitrates after near-UV absorption.

3.4. Atmospheric photodissociation rates

Atmospheric photodissociation rates of 1-propyl, 2-propyl, 1-butyl, and 1-pentyl nitrates were computed using near-UV absorption cross sections determined in the present study and actinic flux estimates of Demerjian et al. [30]. A C₃-C₅ alkyl nitrate photolysis quantum yield of unity was assumed in this estimation. This assumption is reasonable given that photolysis at 308 nm and in the actinic UV $(\lambda \ge 290 \text{ nm})$ involve $n \to \pi^*$ absorption transition followed by dissociation into $RO + NO_2$ products. Calculated diurnally averaged photolysis rates at the Earth's surface and 40° latitude on July 1 are 0.76 \times 10^{-6} , 1.1×10^{-6} , 0.86×10^{-6} , and 0.87×10^{-6} s^{-1} for 1-propyl, 2-propyl, 1-butyl, and 1-pentyl nitrates, which translate into atmospheric lifetimes of about 15.2, 10.5, 13.5, and 13.3 days, respectively. Thus, these C₃-C₅ alkyl nitrates are long-lived and



Fig. 4. Photolysis rates of 2-propyl nitrate as a function of zenith angle at several altitudes calculated using 298K and temperature-dependent cross sections.

may be important in long-range transport of odd nitrogen.

Photodissociation rate constants at various altitudes in the troposphere were also estimated using the temperature-altitude profile of the Standard U.S. Atmosphere [31]. Presented in Fig. 4 are calculated 2-propyl nitrate photolysis rates as a function of zenith angle at 0, 0.98, 5, and 15 km altitude, using 298 K and temperature-dependent cross sections. The estimated tropospheric photolysis rates exhibit a strong dependence on both altitude and temperature. In the Regional Acid Deposition (RADM2) gas-phase chemical mechanism, [32] alkyl nitrates were lumped into a surrogate species with an average of 4 carbon atoms. Alkyl nitrate photolysis rates were calculated using room-temperature methyl and ethyl nitrate absorption cross sections [29]. Since the absorption cross sections of alkyl nitrates are strongly temperature dependent in the actinic UV region, the photolysis lifetimes of alkyl nitrates in the upper troposphere are significantly longer than those calculated using room-temperature alkyl nitrate absorption cross sections. It is therefore essential to incorporate absorption cross section temperature dependence into models such as RADM2 in order to better describe alkyl nitrate chemistry in the atmosphere.

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