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Journal of Photochemistry and Photobiology A: Chemistry 171 (2005) 77–82
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Gas phase UV absorption spectra for a series of alkyl sulfides

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Received 5 August 2004; received in revised form 21 September 2004; accepted 22 September 2004
Available online 11 November 2004

Abstract

Absorption cross-sections have been measured for a series of alkyl sulfides between 209.0 and 235.0 nm. Measurements are reported for dimethylsulfide ($(CH_3)_2S$, h_6-DMS) and its deuterated isotopomer ($(CD_3)_2S$, d_6-DMS), methylethylsulfide ($CH_3SC_2H_5$, MES), diethylsulfide ($(C_2H_5)_2S$, DES), dipropylsulfide ($(C_3H_7)_2S$, DPS) and dibutylsulfide ($(C_4H_{10})_2S$, DBS).

Keywords: Absorption spectra; Alkyl sulfides

1. Introduction

As the largest natural source of reduced sulfur, dimethylsulfide (CH_3SCH_3, DMS) plays a critical role in atmospheric sulfur cycling and has been linked to changing climate [1]. For these reasons, the chemistry of reduced sulfur compounds, most notably DMS, has been a focus of intense laboratory study. The alkyl sulfides are also convenient photolytic precursors of both alkyl and alkylsulfenyl radicals for kinetic and spectroscopic studies; however, accurate absorption cross-sections and quantum yields are required for calculation of radical concentrations. The vacuum-ultra violet (VUV) absorption spectrum of DMS in the wavelength range 190–250 nm was first reported by Thompson et al. [2] and then by Scott et al. [3]. McDiarmid [4] reported observations of the spectra of both h_6-DMS and d_6-DMS between 125 and 250 nm and tabulated the isotope shifts associated with 24 transitions. More recent observations include, Tokue et al. [5], Hearn et al. [6] and a recent high-resolution spectrum from Limão-Vieira et al. [7]. Single, atomic line measurements have been reported in conjunction with kinetic measurements for both isotopomers [8,9].

Spectroscopic data on the larger alkyl sulfides is sparse. A measurement of the UV spectrum of methylethylsulfide ($C_2H_5SCH_3$, MES) between 200.0 and 235.0 nm with a resolution of 0.50 nm was reported by Tycholiz and Knight [10]. Hearn et al. [6] reported a spectrum of diethylsulfide ($(C_2H_5)_2S$, DES) between 200.0 and 280.0 nm with a resolution of 0.1 nm. The UV absorption cross-sections of dipropylsulfide ($(C_3H_7)_2S$, DPS) and dibutylsulfide ($(C_4H_9)_2S$, DBS) have not previously been reported. In addition to spectra, a limited number of absorption cross-section measurements are available at 228.8 and 213.9 nm for h_6-DMS, d_6-DMS, DES and MES [9,10]. These have been reported in conjunction with kinetic measurements, and correspond to the wavelengths of zinc and cadmium atomic lines that are particularly convenient for monitoring sulfide concentrations in kinetic studies. A recent experimental study by Martínez-Haya et al. [11] detail the photodissociation dynamics of both h_6-DMS and d_6-DMS. In this work we report absolute cross-sections for several alkyl sulfides in the wavelength range of 200.0–235.0 nm, including the first reported measurements for d_6-DMS, DPS and DBS.

2. Experimental

Absorption cross-sections were measured between 209.0 and 237.5 nm using a diode array spectrometer. A deuterium

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doi:10.1016/j.jphotochem.2004.09.008

lamp (Hamamatsu L979-01) served as the light source for the array measurements. The light passed through an absorption cell with heated windows and an attached capacitance manometer for pressure measurements. Light was then dispersed by a 0.5 m spectrograph (Jobin–Ivon HR640), detected by a 1024-element photodiode array (EG&G M1421) and processed by an optical multichannel analyzer (OMA, EG&G M1463). The wavelength scale was calibrated using the atomic lines from Zn and Cd lamps (BHK Inc.). With a 3000 lines per mm spectrometer grating, we obtained a resolution of ~0.05 nm, taken from the FWHM of isolated atomic lines. In addition, for h_6-DMS and d_6-DMS, the absorption cross-sections at the 213.9 nm atomic line of Zn and the 228.8 nm atomic line of Cd were measured. For the single line measurements, the attenuation of the atomic line was monitored using a photomultiplier masked by a narrowband dichroic filter of the appropriate wavelength. A 100.3 cm cell was used for all experiments.

Spectra for h_6-DMS, d_6-DMS and MES were measured using a static system. A known pressure of the standard, sulfide/N_2 bulb mixture was introduced into the absorption cell and the attenuation of the deuterium lamp or the atomic line, was monitored as a function of pressure. For DPS and DBS, initial measurements using the neat sulfide suggested significant artifacts due to difficulties in pressure measurement caused by the adherence of the sulfide to the walls. Instead, cross-section measurements were made using very dilute mixtures of DPS and DBS in argon in large pyrex storage bulbs. For DPS and DBS bulbs, known amounts of the liquid sulfide were introduced into pre-filled bulbs containing argon, which were then allowed to mix for 24 h. The concentration of the sulfide was monitored using gas chromatography in conjunction with flame ionization and mass spectrometric detection (GC/FID/MS). After an initial loss of sulfide to the walls, the gas phase concentration stabilized and this mixture was used for absorption measurements. Although, adherence to the cell walls was diminished somewhat with this technique, static measurements using these mixtures were irreproducible. Finally, measurements were made in a flowing system which apparently allowed the cell walls to “condition” and reach a steady state in which absorption and desorption were proceeding at equal rates. This was confirmed by taking 20 scans of optical density as a function of wavelength and ensuring that the wavelength-dependent optical density did not vary significantly over the course of the measurement. Each scan consisted of a 1 min average, ensuring that the concentration was stable over a period of at least 20 min. Spectra of DPS and DBS were obtained using the flowing, dilute mixtures only, while spectra of h_6-DMS and DES were obtained using both the static and flowing methods. Standard mixtures of h_6-DMS, d_6-DMS, MES and DES were made both manometrically and by liquid injection with GC/FID/MS determination of the concentration.

The GC/FID/MS measurements utilized a gas chromatograph (Hewlett-Packard 5890) fitted with a 60 m × 0.25 mm i.d. × 1.4 μm film HP-624 column and both flame ionization (FID) and mass spectrometric (MS) detection were employed. Samples ranging from 10 to 50 cm^3 were concentrated on a silanized glass bead filled, stainless steel loop immersed in liquid argon. Concentrated samples were injected for 2 min at 90 °C. Sample volumes were measured by pressure difference in a previously evacuated volume with a capacitance manometer. The oven temperature program was 35 °C for 6 min followed by a temperature ramp of 20 °C min^{-1} to 190 °C, which was held for 5 min. Both the GC/FID and GC/MS systems were calibrated using single component and multi-component gravimetrically prepared standards that were prepared by NIST or referenced to NIST prepared standards and were cross-calibrated with permeation tubes and/or FTIR spectroscopy.

3. Results and discussion

Absorption cross-sections at each wavelength were calculated using the Beer–Lambert law:

$$\ln\left(\frac{I}{I_0}\right) = lc\sigma \quad (1)$$

where I_0 and I are the measured light intensities through the

Table 1
UV absorption cross-sections for h_6-DMS, d_6-DMS, MES, DES, DPS and DBS. Comparison with previous measurements

Sulfide	$\sigma_{228.8\,nm} \times 10^{-19}$ cm^2	$\sigma_{228.8\,nm} \times 10^{-19}$ cm^2 (this work)	$\sigma_{213.9\,nm} \times 10^{-19}$ cm^2	$\sigma_{213.9\,nm} \times 10^{-19}$ cm^2 (this work)
h_6-DMS	11.6[a], 10.9[b], ~9.6[c], 10.1[d]	10.9 ± 0.25	17.0[e], 16.97[b], ~17.0[c], 14.0[d]	13.6 ± 0.31
d_6-DMS	5.16[a]	5.04 ± 0.01	12.3[e]	11.8 ± 0.08
MES	8.45[a], 7.6[f]	7.34 ± 0.22	19.0[f]	20.0 ± 0.09
DES	9.64[a], 9.15[b]	9.57 ± 0.39	32.6[b]	36.6 ± 0.17
DPS	None	7.50 ± 1.32	None	35.2 ± 3.58
DBS	None	8.47 ± 0.69	None	44.0 ± 2.51

[a] Hynes et al. [9]. Single line measurements reported only.
[b] Hearn et al. [6]. Spectra between 201 and 285 nm.
[c] Thompson et al. [2]. From plot.
[d] Limão-Vieira et al. [7]. High-resolution spectra between 110 and 250 nm.
[e] Barone et al. [8]. Single line measurements reported only.
[f] Tycholiz and Knight [10]. Spectra between 204 and 234 nm.