Impurity contribution to photoabsorption of saturated fatty acids and its implications to tropospheric chemistry

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Saturated fatty acids are abundant surfactants in oceans and sea sprays, in which they concentrate at interfaces. Recent laboratory studies have reported that irradiating liquid saturated fatty acids with ultraviolet (UV) wavelengths longer than 295 nm produce various volatile organic compounds, which enhance marine aerosol formation by acting as precursors [1]. UV absorption spectra of liquid saturated fatty acids exhibit a weak shoulder absorption band centered at 270 nm and extending to 330 nm, in addition to the main band at around 210 nm, due to a singlet-singlet (S_0-S_1) $n\rightarrow\pi^*$ transition (Fig. 1). Various origins have been proposed for shoulder absorption, e.g., carboxylate anions, a singlet-triplet (S_0-T_1) $n\rightarrow\pi^*$ spin-forbidden transition of neutral molecules, and the formation of cyclic dimers [2]. However, no consensus has yet been reached, despite over 90 years of investigation [3].

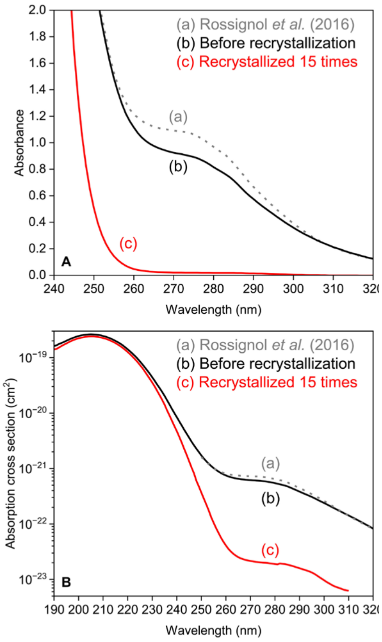

Fig. 1. UV absorption spectra and absorption cross sections of liquid nonanoic acid at room temperature. (A) UV absorption spectra of nonanoic acid: (a) reported by Rossignol et al. [1] for a commercial sample (purity, 97%) and measured here for a commercial sample (purity, >98.0%) (b) before and (c) after recrystallization. Optical path lengths were 10 mm. (B) The corresponding calculated absorption cross sections [3].

The present study of the absorption of wavelengths longer than 250 nm by nonanoic acid [$CH_3(CH_2)_7COOH$], a representative fatty acid present in the sea-surface microlayer, demonstrates that the weak absorption band originates from trace amounts of impurities (0.1% at most) intrinsically contained in nonanoic acid reagents (Fig. 1). We developed a unique recrystallization purification system and purified commercial nonanoic acid by 15 recrystallizations. As a result, the absorption band at 250−330 nm completely disappeared (Fig. 1A). The absorption cross section at 295 nm (1.3×10^{-23} cm^2) was found to be three orders of magnitude smaller than those typical for atmospherically relevant organic molecules such as formaldehyde (H_2CO, 4.4×10^{-20} cm^2), acetaldehyde (CH_3CHO, 4.3×10^{-20} cm^2), and acetone ($CH_3(CO)CH_3$, 3.4×10^{-20} cm^2) at 295 nm (1 nm average) in the gas phase [2]. Our results show that purified fatty acids are photochemically inert in the troposphere, in contrast to previous predictions. This study also suggests that more accurate evaluation about the effects of impurities is required for scientific research. This is particularly important in research of photochemical systems because impurities and contaminants can act as photosensitizers when they are selectively excited by photons.

References

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[3] O. Hartleb, 1931, Strahlentherapie, 39, 442.