WATER RESEARCH 45 (2011) 6535–6544

Available online at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Sorbic acid as a quantitative probe for the formation, scavenging and steady-state concentrations of the triplet-excited state of organic compounds

Janel E. Grebel [a], *Joseph J. Pignatello* [a,b], *William A. Mitch* [a,*]

[a] *Department of Chemical and Environmental Engineering, Yale University, Mason Lab 313b, 9 Hillhouse Ave., New Haven, CT 06520, USA*
[b] *Department of Environmental Sciences, Connecticut Agricultural Experiment Station, 123 Huntington St., New Haven, CT 06504, USA*

ARTICLE INFO

Article history:
Received 20 July 2011
Received in revised form
19 September 2011
Accepted 25 September 2011
Available online 12 October 2011

Keywords:
Triplet
Sorbic acid
Probe
Photochemistry

ABSTRACT

Sorbic acid (*trans,trans*-hexadienoic acid) was developed as a probe for the quantification of the formation rate, overall solution scavenging rate and steady-state concentrations of triplet-excited states of organic compounds. The method was validated against literature data for the quenching rate constant of triplet benzophenone by tyrosine obtained by laser flash photolysis and by Stern–Volmer plots of phosphorescence quenching. In contrast to these methods, the probe method does not require knowledge of the optical properties of triplets to monitor their quenching. Moreover, the probe method permits simultaneous quantification of triplet formation, quenching and steady-state concentrations during illumination of complex chromophore mixtures, such as natural organic matter (NOM), with polychromatic light >315 nm. Application of the method to de-aerated Suwannee River NOM illuminated with polychromatic light (315–430 nm) resulted in a triplet quantum yield of 0.062.

1. Introduction

In organic chromophores, photon absorption by the singlet ground state (S_0) leads to an excited singlet state (S_1) that can relax to the ground state or undergo intersystem crossing (isc) to an excited triplet state (T_1) in which the excited electron has undergone a spin flip (Carroll, 1998). Triplet state chromophores can revert to the ground state (S_0) via a second isc involving an electron spin flip. Considered “spin-forbidden”, isc is a low probability event and characteristically slower than other intersystem processes. Triplet lifetimes (μs-s) are significantly longer than singlet lifetimes (ns-μs) (Turro et al., 2009), and triplets are more likely to engage in photochemical reactions. In the case of direct photolysis, such reactions may lead to chromophore destruction. In the case of indirect photolysis, excited triplet chromophores, particularly chromophoric groups in natural organic matter (NOM), may transform other solution constituents by direct interaction, or by the formation of secondary photo-oxidants (e.g., hydroxyl radical or singlet oxygen).

Previous research has indicated that certain solution components, including dissolved oxygen and halide ions, may affect triplet concentrations by altering intersystem crossing rates ($S_1 \rightarrow T_1$ or $T_1 \rightarrow S_0$), or reacting with triplets (Koziar and Cowan, 1978; Kuzmin and Chibisov, 1971; Treinin et al., 1983; Loeff et al., 1984). We had previously demonstrated that halides enhance the photobleaching of dissolved organic matter, but the mechanism was unclear (Grebel et al., 2009), except that it was not ionic strength-related. Because of the importance of triplets to photochemical processes, a method

---

* *Corresponding author.* Tel.: +1 203 432 4386; fax: +1 203 432 4387.
E-mail address: william.mitch@yale.edu (W.A. Mitch).

0043-1354/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.watres.2011.09.048

that can quantify the effects of solution components on triplet formation and scavenging, as well as quantify their steady-state concentrations, would be a valuable tool toward understanding photochemical reactions in the environment.

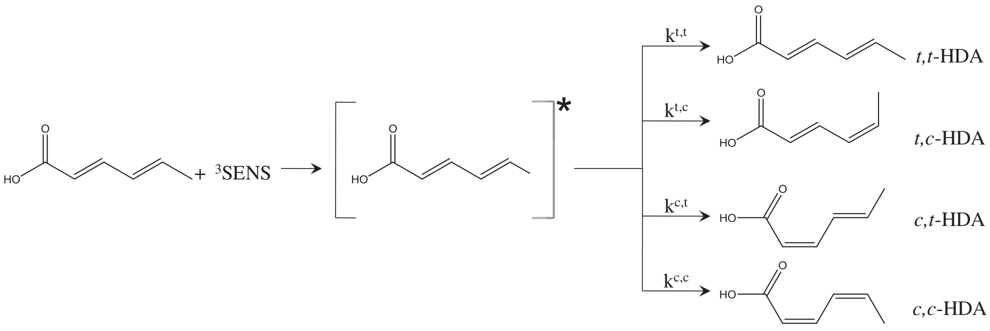
Because organic triplets are present at very low concentrations and have short lifetimes, their measurement requires special analytical techniques. Several studies have examined triplet quenching rates using Stern–Volmer plots of the reduction in phosphorescence upon adding a quenching agent (e.g., Turro and Engel, 1969; Zepp et al., 1985). Unfortunately, this method does not provide information on triplet formation rates or steady-state concentrations. Laser flash photolysis techniques (Canonica et al., 2000), which enable direct detection of triplets by their UV absorbance, have several limitations, especially for the study of natural waters which contain complex mixtures of chromophores (e.g., NOM). Expensive and delicate equipment is required. The decay of only relatively long-lived triplets can be monitored, and their formation rates often cannot be resolved by laser systems. The high photon intensities increase the likelihood of bi-photonic processes, which are not generally important in natural systems. Lasers, although able to scan over a wavelength range, are limited to monochromatic irradiation at any one time. Lastly, it is likely that NOM generates an array of triplets with different absorbance spectra, rendering their quantification by UV absorbance difficult.

In contrast to direct measurement techniques, probe methods employ a chemical that reacts in a characteristic fashion with the species of interest (e.g., excited triplet organics). The probe concentration is low enough to avoid significant system perturbation, yet high enough that the reaction products can be monitored using standard laboratory equipment. The formation of reaction products can be monitored to quantify the rates of formation and removal, as well as the steady-state concentrations of the triplets.

The objective of this study was to develop and evaluate sorbic acid (*trans,trans*-hexadienoic acid, *t,t*-HDA) as a probe of excited triplet chemistry, including solution constituent effects on triplet formation, scavenging and steady-state concentrations. Sorbic acid is an excellent triplet probe for several reasons. First, *t,t*-HDA and other simple dienes have been utilized previously to quench triplet reaction pathways (Zepp et al., 1985; Velosa et al., 2007), but have not been developed as quantitative probes. As a carboxylic acid, sorbic acid is more water-soluble than other diene quenching agents, such as 1,3-pentadiene. Quenching reactions occur when excited state organics transfer energy to the diene. As a result, the excited state organic (sensitizer) reverts to the ground state (S_0), while the diene is promoted to an excited state. Quenching reactions are possible only if the excited state energy of the diene probe is less than the relevant excited state of the sensitizer. With high singlet energies (E_S ~400 kJ/mol) and moderately low triplet energies (E_T ~200–250 kJ/mol), dienes will only interact with the most energetic of singlet sensitizers, but will quench a wide range of triplets (Montalti et al., 2006). Therefore, the technique is selective for quantification of triplet, rather than singlet, excited chromophores. In the case of NOM, previous research indicated that, of the NOM triplets with sufficient energy (94 kJ/mol) to activate dissolved oxygen to singlet oxygen, ~35% had triplet energies of ~250 kJ/mol that could be quenched by dienes (Zepp et al., 1985); these higher energy NOM triplets may be critical for NOM photochemistry.

Second, the interaction of *t,t*-HDA with organic triplets results in HDA isomerization, producing a mixture of *trans–trans*, *trans–cis*, *cis–trans,* and *cis–cis* species (Scheme 1). Other oxidants, such as singlet oxygen and hydroxyl radicals, that potentially react with HDA, will not produce isomer products. Thus, quantification of isomer products, as opposed to *t,t*-HDA loss, ensures the only reaction pathway quantified is that with the desired triplet state organic species. This ability to monitor isomer reaction products is an advantage over other triplet probes. For example, loss of trimethylphenol has been used to probe triplets (Halladja et al., 2007), but because the reaction products are uncharacterized, and trimethylphenol also reacts with other reactive species (e.g., singlet oxygen), it is difficult to link trimethylphenol loss to triplet interactions alone. Third, triplet spectra of particular NOM components or organic compounds, necessary for direct detection in laser-based studies, are not required.

Fourth, the method requires relatively simple apparatus. Samples can be analyzed by high performance liquid chromatography with ultraviolet detection (HPLC–UV). Fifth, low wattage or natural light sources can be used for irradiation. Users are able to experiment with true polychromatic irradiation, resulting in more realistic excitation conditions. For NOM, Zepp et al. (1985) found that NOM triplet energies varied with irradiation wavelength. Variations in energy of the photons absorbed led to excitation to different excited states, underscoring the importance of using the most realistic polychromatic irradiation conditions feasible. Lastly, because *t,t*-HDA absorbs only weakly in the near ultraviolet, and not at



Scheme 1 – Products of interaction between triplet-excited organic sensitizer and sorbic acid (*trans-trans*-HDA).