

Femtosecond to microsecond observation of photochemical reaction mechanisms

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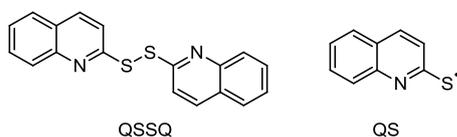
Introduction

Many chemical reactions in solution are initiated by absorption of ultraviolet (UV) or visible light. The energy of the absorbed light can prepare reactive excited states, or cause chemical bonds to break, creating free radicals with unpaired electrons. Subsequent chemical reactions may involve multiple, sequential steps, such as in radical chain or polymerization reactions. The steps involving bimolecular reactions are typically much slower than the photochemical initiation, and they may be limited by the timescales for diffusive encounters with co-reactants, or thermal activation to overcome an energy barrier associated with a reaction transition state. The study summarized here illustrates how the LIFETIME laser system at the ULTRA facility can be used to track several sequential reaction steps spanning time intervals from 200 fs to 50 μ s, thereby giving a complete picture of the production and loss of reactive intermediates such as free radicals.

The system chosen for study was an example of thiol-ene reaction, an important class of radical addition reactions in which a thiyl radical (RS^\bullet) reacts with an alkene. Thiol-ene reactions have been studied for more than a century [1], and they are important in industrial applications such as light-curing of resins or vulcanization in the rubber industry. With the growing popularity of "Click-Chemistry" [2], they have experienced a resurgence of interest in synthetic chemistry. A combination of transient electronic absorption spectroscopy (TEAS) and transient vibrational absorption spectroscopy (TVAS) provides a detailed picture of the reaction mechanism from photolytic production of the thiyl radicals through to their reactions with alkenes, and the subsequent fates of the radical adducts formed [3].

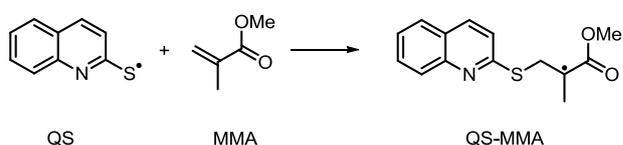
Methodology

The thiyl radicals were produced by photolysis of a disulfide compound, using ultrafast UV laser pulses at a wavelength of 320 nm. The disulfide 1,2-di(quinoline-2-yl)disulfide (QSSQ) was used as a precursor for the quinoline-2-thiyl (QS) radical. Experiments were carried out using either methanol or deuterated chloroform as a solvent, and methyl methacrylate (MMA) was chosen as the alkene participant in the thiol-ene reaction because of its IR-active carbonyl group. The structures of QSSQ and QS are shown below, together with the expected addition reaction of QS with MMA.



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The QS radical has a characteristic absorption spectrum in the visible region, which can be observed by TEAS using a white-light continuum generated in a CaF_2 optic. TVAS in the 1075 – 1700 cm^{-1} using the LIFETIME laser system provides a remarkably complete picture of the radical chemistry initiated by QS production in the presence of MMA.

Results

Transient electronic absorption spectra of the type shown in Figure 1 illustrate the ultrafast production of QS radicals by QSSQ photolysis, in this case in methanol. The radicals decay with exponential time constants of 3.5 ps and 110 ps corresponding to geminate and diffusive recombination of radical pairs to re-form the parent QSSQ. Only about 36% of the initially formed radicals survive this recombination for 1 ns or longer.

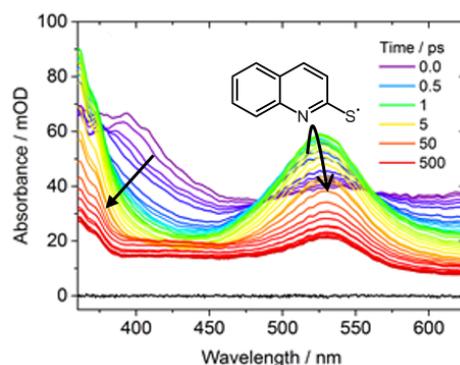


Figure 1: Transient electronic absorption spectra showing production and decay of QS radicals from 330-nm excitation of a 1.0 M solution of QSSQ in methanol. The colours indicate spectra obtained at different time delays, as indicated in the inset key. The black trace is a baseline measurement. The band centred at 525 nm is assigned to the QS radical. The black arrows show the directions of change with time of transient absorption features.

On addition of MMA, the QS band decays to zero, on a time scale controlled by the MMA concentration, because of loss by both recombination to QSSQ and bimolecular addition to MMA. Signatures of this reaction mechanism are more evident in TVAS data, and an example set of transient spectra obtained with an IR probe is shown in Figure 2.

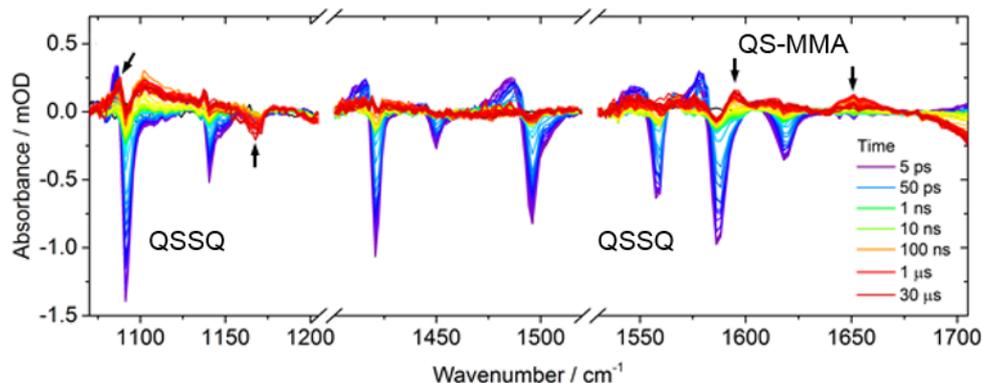
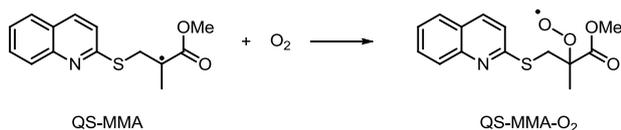


Figure 2: Transient vibrational absorption spectra obtained for a 3.8 mM QSSQ and 100 mM MMA solution in CDCl_3 following 330 nm excitation. The spectra were obtained over time delays from 5 ps to 30 μs , as shown by the inset key. Band assignments are discussed in the main text.

The TVAS data are rich in chemical information. Negative going “bleach” features at 1091, 1141, 1421, 1450, 1496, 1558, 1586 and 1618 cm^{-1} in Figure 2 correspond to QSSQ, which is depleted by the UV excitation pulse and reforms on timescales of a few picoseconds by recombination of QS radicals. The recovery times of the bleach features are largely controlled by vibrational relaxation of the highly internally excited QSSQ molecules, which are the initial products of recombination of a pair of QS radicals. The negative features at 1168 cm^{-1} and around 1700 cm^{-1} develop at later times and are caused by reactive depletion of MMA.

Five bands evident in Figure 2 can be assigned to reaction products. These lie at 1088, 1102, 1137, 1595, and 1653 cm^{-1} , and some are indicated by black arrows in the figure. Under the conditions of the experimental measurements, they grow with time constants of 100 ns. These bands are assigned to the QS-MMA radical (see above), on the basis of electronic structure calculations of vibrational frequencies of this reactive intermediate. For example, the 1653 cm^{-1} band is associated with the C=O stretch of this radical adduct, and is shifted to lower wavenumber than the carbonyl stretch in MMA because of conjugation with the adjacent radical centre. After reaching a maximum intensity at a time delay of ~ 300 ns, this band decays over the full temporal window of 50 μs because of reactive loss of the QS-MMA radical. One candidate for its removal is reaction with dissolved oxygen to make a peroxy radical species QS-MMA- O_2 (see below). This species is computed to have IR-active vibrational modes underlying the QS-MMA absorption bands at 1088 and 1595 cm^{-1} , which accounts for the persistence of these spectral features while the 1653 cm^{-1} QS-MMA band decays. This pathway was confirmed by repeating the TVAS measurements with solutions purged of dissolved O_2 .



Further analysis of the data indicates that the reaction of QS-MMA with dissolved O_2 to make QS-MMA- O_2 is reversible. Fitting of the time-dependent intensities of the bands in the TVA spectra provides a suite of unimolecular and bimolecular rate coefficients for the various reactions taking place in the UV-excited solutions.

Conclusions

The extended measurement time capability of the LIFETIME instrument, covering ultrafast (sub picosecond) to microsecond time delays in a single set of measurements, provides an unprecedented capability to track the production and loss of short-lived reactive intermediates. This capability is illustrated in the current study by a multi-step photochemical and reactive process. QS thiyl radicals are produced in less than 1 ps by UV excitation of QSSQ disulfide precursor molecules dissolved in CDCl_3 , and undergo bimolecular addition reactions with MMA, chosen as a representative alkene, on nanosecond timescales. The resulting adduct radicals, QS-MMA, are also identified by transient vibrational spectroscopy, and are seen to undergo reversible addition reactions with dissolved oxygen. These preliminary studies of multi-step reaction mechanisms by direct observation of reactive intermediates open up a host of further reactions for possible study, for example including those initiated using photoredox catalysts [4].

Acknowledgements

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