Observation of multiple steps in radical reactions on femtosecond to microsecond timescales

Contact *a.orr-ewing@bristol.ac.uk*

D. Koyama
University of Bristol
School of Chemistry, Cantock's Close, Bristol BS8 1TS

P.M. Donaldson
Central Laser Facility, Science and Technology Facilities Council, Rutherford Appleton Laboratory, Harwell Oxford, Didcot OX11 0QX

A.J. Orr-Ewing
University of Bristol
School of Chemistry, Cantock's Close, Bristol BS8 1TS

Introduction

Radical reactions can be useful tools in organic synthesis, but the possibility of unwanted propagation and chain-transfer reactions limits their widespread use. Thiol-ene reactions represent one synthetically useful class of radical reactions; they can be carried out under mild conditions, and are finding applications in, for example, click chemistry [1]. These reactions involve addition of a thiyl radical (RS·) to an alkene or alkyne. The radical production and reaction steps occur on very different timescales: for example, ultraviolet photolysis of a disulfide compound RSSR produces RS· radicals on sub-picosecond timescales [2], and those radicals which avoid geminate recombination react with co-solute alkenes on nanosecond or longer timescales with diffusion or activation limited rate coefficients. The addition product is itself a radical species, and will either chain terminate by radical recombination, react further with an alkene molecule, or add dissolved oxygen to make a peroxy radical species. The complexity of these competing pathways is hard to unravel because of the distinct timescales for the different steps. We have used the LIFEtime facility at the Research Complex at Harwell, in combination with measurements made on an ultrafast laser system at the University of Bristol [3], to observe thiol-ene reactions over six orders of magnitude of time (sub-picosecond to 50 µs): characteristic infra-red (IR) absorption bands allow the formation and reactive removal of intermediate species to be tracked over several sequential steps in the reaction [4].

Results and Discussion

The thiol-ene reaction chosen for study was between quinoliene-2-thiyl (QS) and methyl methacrylate (MMA). The QS radicals were generated by 330-nm UV photolysis of 1,2-di(quinolin-2-yl)disulfide (QSSQ). The structures of these molecules and radicals, and the thiol-ene reaction of interest, are shown in Figure 1.

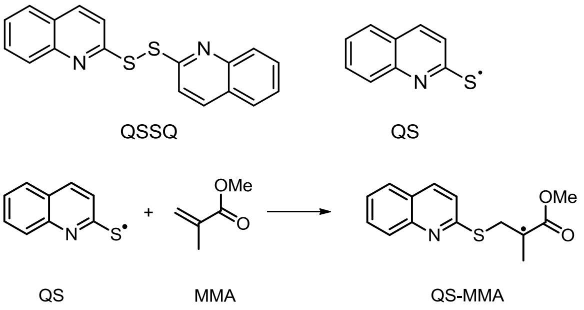

Figure 1: Structures of 1,2-di(quinolin-2-yl)disulfide (QSSQ), quinoliene-2-thiyl (QS) and methyl methacrylate (MMA), and a scheme for the first addition step in the thiol-ene reaction investigated.

Transient electronic absorption (TEA) spectra in the near-UV and visible regions of the spectrum are shown in Figure 2 and confirmed the sub-picosecond formation of QS radicals from QSSQ photolysis at 330–nm. The characteristic absorption band of the QS radical centred at 525 nm decays with two time constants corresponding to geminate recombination and diffusive reaction with MMA. However, the TEA spectra do not definitively reveal the products of the reaction. Transient vibrational absorption (TVA) spectroscopy in the infra-red region was therefore used to provide specific information on reaction intermediates and their fates.

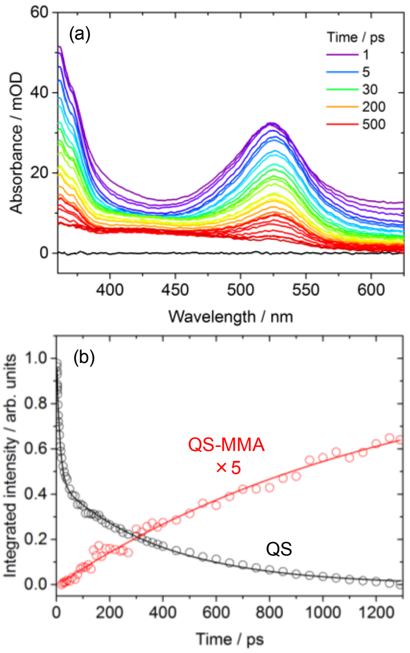

Figure 2: Production and loss of QS radicals in a QSSQ solution in MMA excited at 330 nm. (a) Transient electronic absorption spectra, showing the prompt formation and subsequent decay of a band centred at 525 nm which is assigned to QS· radicals. (b) The time-dependence of the integrated intensity of the QS absorption band, and growth of a weak feature centred near 425 nm which is assigned to the QS-MMA adduct on the basis of evidence from TVA measurements.

TVA spectra were collected across the 1075 – 1700 cm^{-1} range, and a composite set of spectra is shown in Figure 3. The broad wavenumber coverage reveals peaks assigned to depletion of the parent QSSQ molecules by the 330-nm laser pulses, formation and decay of QS· radicals, reactive loss of MMA, and accumulation of QS-MMA adducts.

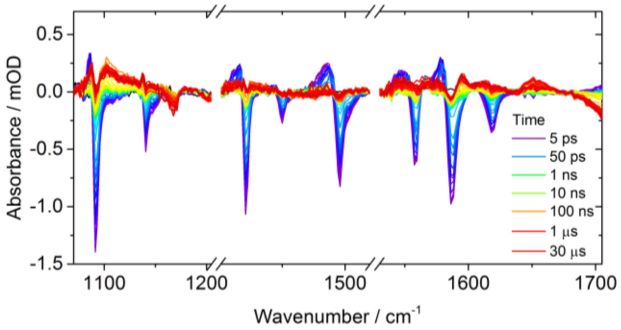

Figure 3: Time-resolved vibrational spectra of a QSSQ (3.8 mM) and MMA (100 mM) solution in $CDCl_3$ obtained after 330-nm excitation. Spectra obtained with the LIFEtime laser system span time delays up to 30 µs, as shown by the inset colour key.

The TVA measurements were conducted for aerated solutions of QSSQ and MMA in $CDCl_3$ and for solutions purged by nitrogen. The differences between results obtained in these solutions are illustrated by the plots of time-dependent band intensities in Figure 4. In particular, the decay of the band at 1635 cm^{-1} assigned to the QS-MMA adduct after 500 ns in the aerated solution, and the absence of this decay in the N_2-purged solution, is attributed to formation of a QS-MMA-O_2 peroxy radical species, corresponding to observation of a third step in the reaction sequence. Further analysis of the time dependence of all the spectral bands provides a comprehensive set of rate coefficients for the various reactions occurring in the QSSQ / MMA / $CDCl_3$ solution [4].

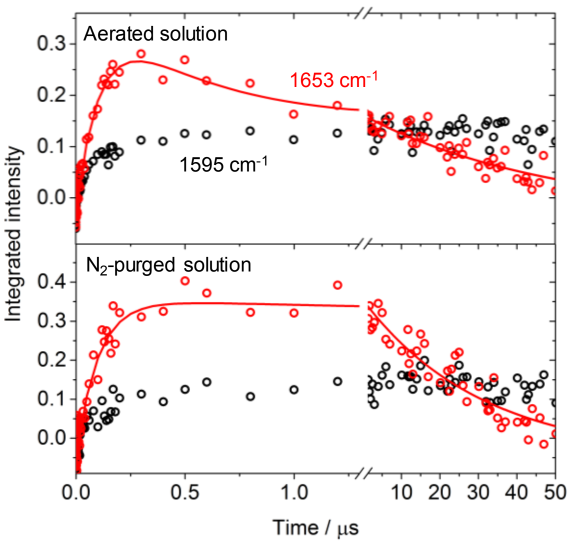

Figure 4: Time-dependence of the integrated band intensities for features in the TVA spectra of a 3.8 mM QSSQ and 100 mM MMA solution in $CDCl_3$ after UV excitation at 330-nm.

Conclusions

The capability of the LIFEtime system to span time delays in photo-initiated reactions from 100 fs to more than 100 µs allows sequences of steps, beginning with the ultrafast initiation of bimolecular radical reactions, to be observed for the first time. This powerful capability is expected to offer new mechanistic insights into a wide range of photochemically driven reactions [5], and will perhaps allow future observation of full catalytic cycles.

Acknowledgements

The Bristol group thanks the European Research Council (ERC Advanced Grant 290966 CAPRI) for financial support. We are grateful to H.J.B. Marroux and K. Röttger for assistance with collection of the experimental data, and D. Murdock for advice on the electronic structure calculations.

References

1. H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem. Int. Ed.*, 2001, **40**, 2004-2021.
2. D. Koyama and A. J. Orr-Ewing, *Phys. Chem. Chem. Phys.*, 2016, **18**, 12115-12127.
3. G. M. Roberts, H. J. B. Marroux, M. P. Grubb, M. N. R. Ashfold and A. J. Orr-Ewing, *J. Phys. Chem. A*, 2014, **118**, 11211-11225.
4. D. Koyama, P.M. Donaldson and A.J. Orr-Ewing, manuscript submitted.
5. D. Koyama, H.J.A. Dale and A.J. Orr-Ewing, unpublished results.