

Application of a novel multipass, broadband time-resolved absorption spectrometer to the study of peroxy radicals: The effect of substitution on kinetics and absorption spectra.

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The distinctive features of this new absorption system are the long path length and high light throughput to the CCD chip detector, which facilitates the very high sensitivity demonstrated by the instrument, which has demonstrated the ability to measure time-resolved (0.8 ms max time resolution) absorptions of less than 0.0005. The mirror arrangement is such that the overlap between the broadband probing light from a Laser Driven Light Source (LDLS) or Xe-Arc lamp and an excimer pulse at 248nm is maximized, providing an efficient way of obtaining the absorption signal whilst minimizing losses in probe intensity.

One application of the instrument has been the study of the kinetics and spectroscopy of peroxy radicals. OH addition and subsequent addition of O₂ is the major sink for isoprene in the atmosphere. The isoprene hydroxyperoxy (HP) radical has 6 possible isomers, of which 1 is tertiary, 2 are secondary and 3 are primary. 2,3 dimethyl butadiene (methyl isoprene) and butadiene are symmetrical dienes which each produce 3 (hydroxyperoxy) HP radical isomers, each mimicking 3 out of the 6 isoprene HP radical isomers. The analogous isoprene, butadiene and methyl isoprene HP radical spectra give absorption cross-sections with a magnitude in the order methyl isoprene > isoprene > butadiene, and since the structures of these molecules are very similar, it follows that the difference seen in their absorption spectra is due to the relative abundances of tertiary, secondary and primary HP radical isomers. The HP radicals of ethylene and tetra methyl ethylene (TME) show a similar trend, in that the tertiary TME HP radical has a much larger (up to 3 fold larger) cross section than the primary ethylene HP radical. "Red shifting" is also observed, whereby the absorption cross sections of the more substituted peroxy radicals decrease more slowly as wavelength is increased, and is observed to be increasingly present in the series methyl isoprene > isoprene > butadiene. As has been observed previously, the degree of substitution also has a strong effect on the rate of the self-reaction between peroxy radicals (>10 fold decrease in rate between primary and tertiary in some cases); the more substituted a peroxy radical, the slower its self-reaction rate, although further analysis is required to quantify the isomer specific self-reaction rates.