

# Peroxy Radical Kinetics using the $\tilde{A} \leftarrow \tilde{X}$ Transition

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Organic peroxy radicals are ubiquitous intermediates in both atmospheric and combustion chemistry. Their competing fates can terminate or propagate free radical chemistry in an oxidation mechanism. Most kinetic data on peroxy radical reactions come from absorption spectroscopy experiments utilizing the  $\tilde{B} \leftarrow \tilde{X}$  transition in the UV. However, the  $\tilde{B}$  state of peroxy radicals is dissociative and leads to broad, overlapping spectra that make elucidating concentration profiles of individual peroxy radicals a challenge for realistic oxidation systems. Over the past two decades, there has been a substantial effort to acquire spectra of the forbidden  $\tilde{A} \leftarrow \tilde{X}$  transition in the near-IR (1). The  $\tilde{A}$  state of peroxy radicals is bound and leads to detailed absorption spectra that vary with molecular structure. Therefore, the  $\tilde{A} \leftarrow \tilde{X}$  transition may be useful in unraveling the kinetics of mixtures of organic peroxy radicals derived from complex hydrocarbons, such as isoprene, where multiple isomers form upon oxidation. Furthermore, absorption by HO<sub>2</sub>, a byproduct of almost all organic peroxy radical chemistry, is well isolated. Despite the promise of this approach, prior kinetic studies utilizing the  $\tilde{A} \leftarrow \tilde{X}$  transition are scarce and have focused on small, unsubstituted peroxy radicals and proof-of-concept systems (2–4). The true potential of the  $\tilde{A} \leftarrow \tilde{X}$  transition remains unexplored. In this work, we investigate the ability of this transition to unravel complex peroxy radical kinetics through experiments on the chlorine-initiated oxidation of alkenes. Atomic chlorine is a minor tropospheric oxidant, found in marine and coastal regions, that reacts with alkenes to yield chlorine-substituted peroxy radicals. We use cavity ringdown spectroscopy in the near-IR spectral region to monitor the growth and decay of peroxy radical absorption features under varying radical environments. We first present rate constants for the self and cross reactions of  $\beta$ -chloroethylperoxy and HO<sub>2</sub>, measured using the isolated absorption signals for these species afforded by the  $\tilde{A} \leftarrow \tilde{X}$  transition. The experiment also provides an unconventional method for determining the  $\beta$ -chloroethylperoxy self reaction branching ratio. We then present kinetic measurements on C<sub>3</sub>–C<sub>5</sub> alkenes and dialkenes that yield multiple peroxy radical isomers upon oxidation. A prevailing assumption in atmospheric mechanisms is that peroxy radical isomers derived from a common parent hydrocarbon react with NO at the same rate. Our time-resolved measurements of  $\tilde{A} \leftarrow \tilde{X}$  absorption spectra suggest isomer-dependent reactivity, and indicate that this assumption may not hold true for isoprene oxidation.

## References

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