Quantitative Kinetic Analysis and Solvent Effects of Hydrogen Transfer Reactions

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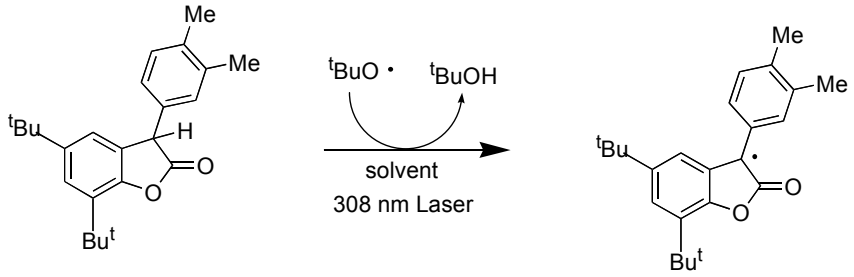
Antioxidants function on the basis of efficient hydrogen transfer. The radical derived from the antioxidant must be relatively unreactive towards oxygen in order to inhibit the autoxidative chain.

The solvent effects on the rate constant of hydrogen abstraction (k_H) from HP-136, an antioxidant based on the formation of a carbon centered radical that does not react with oxygen, are investigated. The radicals are generated by use of *tert*-butoxyl radicals obtained by laser excitation of di-*tert*-butyl peroxide, using 308nm laser pulse. It is shown that k_H is dependent on both: the polarity of the solvent ($E_T(30)$) and the hydrogen bond accepting properties (β_2^H) of the solvent. As well, the rate constant of quenching for HP-136 radical by TEMPO in different solvent environments permits us to discuss the stability of the HP-136 radical in different media.



The absolute k_H from a number of molecules that produce carbon-centered and nitrogen-centered radicals are also reported. These molecules included 2-benzoxazolinone, oxindole, and 3-phenyl-5-isoxazolone. The radicals formed do not show reactivity towards oxygen and their stabilities are discussed in terms of quenching by TEMPO and spin density calculations. Another methodology used to study hydrogen abstraction process involved a series of dietary polyphenols using a pre-fluorescent TEMPO probe. The TEMPO compound is employed as a good model for peroxyl radicals. The polyphenols explored are quercetin, rutin, and caffeic acid, using trolox as a standard phenol. The probes employed in this study are quinoline-TEMPO (QT) and a coumarine-TEMPO (C343T). This methodology works by an intramolecular quenching of the fluorescent properties of the chromophore by the paramagnetic TEMPO moiety attached. Upon hydrogen transfer from the phenol to the nitroxide radical the fluorescence is restored. This allows the rate of hydrogen transfer to be followed directly from the fluorescence growth of the probe. Rate constants on the order of 0.002 – 0.1 $M^{-1}s^{-1}$ are reported. Also, the deuterium kinetic isotopes effect confirms that the mechanism follows a hydrogen transfer process.