Spectral probe for electron transfer and addition reactions of azide radicals with substituted quinoxalin-2-ones in aqueous solutions

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Abstract
The azide radical (N3\(^{\bullet}\)) is one of the most important one-electron oxidants used extensively in radiation chemistry studies involving molecules of biological significance. Generally, it was assumed that N3\(^{\bullet}\) reacts in aqueous solutions only by electron transfer. However, there were several reports indicating the possibility of N3\(^{\bullet}\) addition in aqueous solutions to organic compounds containing double bonds. The main purpose of this study was to find an experimental approach that allows a clear assignment of the nature of obtained products either to its one-electron oxidation or its addition products. Radiolysis of water provides a convenient source of one-electron oxidizing radicals characterized by a very broad range of reduction potentials. Two inorganic radicals (SO\(_4^{\bullet-}\), CO\(_3^{\bullet-}\)) and Ti\(^{2+}\) ions with the reduction potentials higher, and one radical (SCN)\(_2^{\bullet-}\) with the reduction potential slightly lower than the reduction potential of N3\(^{\bullet}\) were selected as dominant electron-acceptors. Transient absorption spectra formed in their reactions with a series of quinoxalin-2-one derivatives were confronted with absorption spectra formed from reactions of N3\(^{\bullet}\) with the same series of compounds. Cases, in which the absorption spectra formed in reactions involving N3\(^{\bullet}\) differ from the absorption spectra formed in the reactions involving other one-electron oxidants, strongly indicate that N3\(^{\bullet}\) is involved in the other reaction channel such as addition to double bonds. Moreover, it was shown that high-rate constants of reactions of N3\(^{\bullet}\) with quinoxalin-2-ones do not ultimately prove that they are electron transfer reactions. The optimized structures of the radical cations (7-R-3-MeQ)*\(^{\bullet}\), radicals (7-R-3-MeQ)* and N3\(^{\bullet}\) adducts at the C2 carbon atom in pyrazine moiety and their absorption spectra are reasonably well reproduced by density functional theory quantum mechanics calculations employing the \(\omega\)B97XD functional combined with the Dunning's aug-cc-pVTZ correlation-consistent polarized basis sets augmented with diffuse functions.

Author keywords
Addition
Azide radical
DFT and TD-DFT calculations
Electron transfer
One-electron radical oxidants
Pulse radiolysis
Quinoxalin-2ones