Plastoquinol generates and scavenges reactive oxygen species in organic solvent: Potential relevance for thylakoids

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Plastoquinol generates and scavenges reactive oxygen species in organic solvent: potential relevance for thylakoids

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Abstract

The present work reports reactions of plastoquinol (PQH_2-9) and plastoquinone (PQ-9) in organic solvents and summarizes the literature to understand similar reactions in thylakoids. In thylakoids, PQH_2-9 is oxidized by the cytochrome b_6/f complex (Cyt b_6/f) but some PQH_2-9 is also oxidized by reactions in which oxygen acts as an electron acceptor and is converted to reactive oxygen species (ROS). Furthermore, PQH_2-9 reacts with ROS. Light enhances oxygen-dependent oxidation of PQH_2-9. We examined the oxidation of PQH_2-9 via dismutation of PQH_2-9 and PQ-9 and scavenging of the superoxide anion radical ($O_2^{\bullet-}$) and hydrogen peroxide (H_2O_2) by PQH_2-9. Oxidation of PQH_2-9 via dismutation to semiquinone was slow and independent of pH in organic solvents and in solvent/buffer systems, suggesting that intramembraneous oxidation of PQH_2-9 in darkness mainly proceeds via reactions catalyzed by the plastid terminal oxidase and cytochrome b_{559}. In the light, oxidation of PQH_2-9 by singlet oxygen and by $O_2^{\bullet-}$ formed in PSI contribute significantly. In addition, Cyt b_6/f forms H_2O_2 with a PQH_2-9 dependent mechanism. Measurements of the reaction of $O_2^{\bullet-}$ with PQH_2-9 and PQ-9 in acetonitrile showed that $O_2^{\bullet-}$ oxidizes PQH_2-9, forming PQ-9 and several PQ-9-derived products. The rate constant of the reaction between PQH_2-9 and $O_2^{\bullet-}$ was found to be 10^4 M^{-1} s^{-1}. H_2O_2 was found to oxidize PQH_2-9 to PQ-9, but failed to oxidize all PQH_2-9, suggesting that the oxidation of PQH_2-9 by H_2O_2 proceeds via deprotonation mechanisms producing PQH^--9, PQ^{2-}-9 and the protonated hydrogen peroxide cation, $H_3O_2^+$.

Keywords: Hydrogen peroxide, plastoquinone, singlet oxygen. superoxide anion radical, thylakoid membrane.

Abbreviations: Chl, chlorophyll; Cyt b_{559}, cytochrome b_{559}; Cyt b_6/f, cytochrome b_6/f complex; DMSO, dimethylsulfoxide; DNP-INT, 2-iodo-6-isopropyl-3-methyl-2',4,4'-trinitrodiphenyl ether; DCMU, 3-(3,4-Dichlorophenyl)-1,1-dimethylurea; HEPES, 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid; $HO_2^{\bullet}$, hydroperoxyl radical; HPLC, high performance liquid chromatography; MeOH, methanol; MES, 2-(N-morpholino)ethanesulfonic acid; $^1O_2$, singlet oxygen; $O_2^{\bullet-}$, superoxide anion radical; P_{680}, primary electron donor of PSII; $PQH^{\bullet}$-9 and $PQ^{\bullet-}$-9 , plastosemiquinone radical and plastosemiquinone anion radical, respectively; PQH_2-9 and PQ-9, plastoquinol and