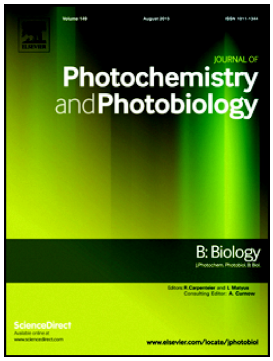

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Exploring the reactivity of retinol radical cation toward organic and biological molecules: a laser flash photolysis study

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Abstract

Vitamin A (retinol) and various natural retinoids are essential for life. Under oxidative conditions, vitamin A radical cation ($RET^{\bullet+}$) can be formed. Many deleterious effects were reported about the formation of carotenoid radical cations in biological environments, on the other hand, little is known about the consequences of the $RET^{\bullet+}$ formation in these environments. Therefore, it is important to explore the reactivity of $RET^{\bullet+}$ toward various biological substrates. Here, we employed nanosecond laser flash photolysis (LFP) to generate $RET^{\bullet+}$ (λ_{max} = 580 nm in methanol) and examine its reactivity toward a wide range of biological molecules including amino acids, vitamins, carotenoids, naturally-occurring phenols, neurotransmitters such as catecholamines, wide range of phenol derivatives and some selected electron-donors. The results show that the reactivity of $RET^{\bullet+}$ toward various substrates is strongly dependent on the polarity of solvent. In addition, $RET^{\bullet+}$ is able to oxidize amino acids, which subsequently can lead to protein damage. However, the presence of vitamins (vitamins E and C), carotenoids and naturally-occurring phenols (*e.g.* resveratrol, vanillin, dopamine hydrochloride and L-Dopa) can inhibit the damaging effect of retinol$^{\bullet+}$ by reducing it back to retinol. Vitamin E and carotenoids are the most efficient quenchers for the $RET^{\bullet+}$ (diffusion-controlled reactions). Importantly, our results clearly indicate that the reactivity of $RET^{\bullet+}$ is as strong as that of the powerful trichloromethylperoxyl radical ($CCl_3O_2^{\bullet}$). Thereby, formation of $RET^{\bullet+}$ in biological media is expected to induce bio-damage.

Keywords: Retinol radical cation; amino acids; vitamins; carotenoids; phenols; laser flash photolysis.