

Reaction of β -Carotene with Nitrite Anion in a Homogeneous Acid System. An Electron Paramagnetic Resonance and Ultraviolet-Visible Study

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Abstract. Ultraviolet and visible spectroscopy was applied to characterize and to measure the concentration of β -carotene dissolved in a dioxane and water mixture. The reaction of β -carotene in the presence of nitrite anion and acid medium was studied at different temperatures. The reaction systems were homogeneous and were kept anaerobic. Pseudo-first-order rate constants in respect of β -carotene were measured in the range from 293 to 313 K and pH 5.8 ± 0.2 . The energy of activation was calculated to be $E_a = 67.2 \pm 3.4$ kJ/mol. We interpolate a value that may have biological interest, $k_{\beta\text{-carotene}}(310\text{ K}) = (9.70 \pm 0.78) \cdot 10^{-3} \text{ s}^{-1}$, in the presence of $9.3 \cdot 10^{-3}$ M nitrite anion. Electron paramagnetic resonance spectroscopy was applied to characterize and quantify a persistent intermediate radical generated in the reaction system described. The recorded spectra showed triplet-type signals with a peak-to-peak value of 12.7 G. Nearly the same triplet radical-type intermediates were detected when studying the following reaction systems in pure dioxane: nitrogen dioxide (NO_2)/ β -carotene, nitric oxide (NO)/ β -carotene and NO/NO_2 / β -carotene. Therefore, we proposed that the nitrogen oxides have also been intermediates in the reaction system of β -carotene, nitrite anion and acid medium, in the dioxane and water mixture. A mechanism was proposed and checked by employing the chemical kinetics simulation. The explanations developed would lead to a better understanding of the behavior of carotenoids in the presence of nitrite anion and nitrogen oxides.

1 Introduction

The reaction of free radicals with carotenoids and the properties of carotenoid free radicals are of great interest because of their potential role in biological systems, in particular their antioxidant and prooxidant properties. We have carried out our work only with β -carotene, an unsaturated and extensively conjugated hydrocarbon. It has been found that carotenes in combination with α -tocopherol reduce radiation effects in normal tissues. Moreover, consistent with its protec-