CHEMILUMINESCENCE OF TRYPTOPHAN HYDROPEROXIDES

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Exposure of proteins to reactive oxygen species can give rise to modifications in amino acids backbone and / or side chain. It has been shown that tryptophan (W) is one of the most vulnerable amino acids, yielding hydroperoxides (WOOH) as primary products. These hydroperoxides are relatively stable, but can decompose under heating and pH changes. In the present work, we are interest in the chemiluminescence (CL) generated by WOOH decomposition. WOOH were synthesized and analyzed by HPLC / MS / MS and NMR. Light emission was measured with a red-sensitive photomultiplier tube cooled to - 20 °C. Two different conditions were employed: first, WOOH (3 mM) were heated to 70 °C and the CL was monitored over a period of time. The second experiment was carried out injecting NaOH (final concentration 20 mM) into WOOH solution (3 mM) and monitoring the light emission. The results show that upon heating or basification the hydroperoxides decompose generating CL. HPLC /MS analysis of the reactions identified N-formylkynurenine (FMK) as a decomposition product. A possible route leading to light emission is the WOOH decomposition via an intermediate dioxetane. This intermediate cleaves in an excited FMK that return to ground state emitting light.

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