

Sensitized photooxidation of thyroidal hormones. Evidence for heavy atom effect on singlet molecular oxygen [$O_2(^1g)$]-mediated photoreactions

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Thyronine derivatives are essential indicators of thyroid gland diseases in clinical diagnosis and are currently used as standards for developing ordinary biochemical assays. Photo-oxidation of gland hormones of the thyronine (TN) family and structurally related compounds (TN, 3,5-diiodothyronine, 3,3',5'-triiodothyronine and 3,3',5,5'-tetraiodothyronine or thyroxine) was studied using rose bengal, eosin and perinaphthenone (PN) as dye sensitizers. Tyrosine (Tyr) and two iodinated derivatives (3-iodotyrosine and 3,5-diiiodotyrosine) were also included in the study for comparative purposes. Irradiation of aqueous solutions of substrates containing xanthene dyes with visible light triggers a complex series of competitive interactions, which include the triplet excited state of the dye ($^3X_{dye}^*$) and singlet molecular oxygen [$O_2(^1g)$]- mediated and superoxide ion-mediated reactions. Rate constants for interaction with the $^3X_{dye}^*$, attributed to an electron transfer process, are in the order of