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DYE-SENSITIZED PHOTOOXYGENATION OF N,N-DIMETHYLBENZYLAMINE. SINGLET-OXYGEN PROCESS IN COMPETITION WITH TYPE I PROCESS(1)

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Dye-sensitized photooxygenation of N,N-dimethylbenzylamine was shown to proceed by both singlet-oxygen and Type I mechanisms. The efficiency of each process was found to be strongly dependent on the type of photosensitizer.

It has long been known that the photooxygenation of amines, to give aldehydes and other products, can be sensitized by dyes.(2) Although tertiary amines have been well established to react with singlet oxygen and/or quench it without reaction,(3) some confusion has still existed about the mechanism of the dye-sensitized photooxygenation. Bartholomew and Davidson have reported that the dye-sensitized photooxygenation of tertiary amines porceeds by a non-singlet-oxygen mechanism (Type I mechanism) in which the primary photoreaction is abstraction of hydrogen from amines by triplet state of the dye.(4) We wish to report that the dye-sensitized photooxygenation of N,N-dimethylbenzylamine proceeds by both a singlet-oxygen mechanism and a Type I mechanism.

Photosensitized oxygenation of N,N-dimethylbenzylamine (1) (5.9×10^{-2} M) in the presence of rose bengal (1×10^{-4} M) in methanol gave two major products, benzaldehyde (2) and N-benzyl-N-methylformamide (3), together with small amounts of minor products. As a check for singlet-oxygen participation in the reaction, we tested the inhibitory effects of known singlet-oxygen quenchers, β-carotene,(5) DABCO,(6) and NaN_3(7) on the rate of the disappearance of 1. The rate (R_q) of the photooxygenation in the presence of varying amounts of quenchers was compared with that of the control experiment (R_o)(Fig. 1). The ratio (R_q/R_o) decreases with increasing the concentration of β-carotene or DABCO, and at higher concentrations the value ($R_q/R_o = 0.80$) is independent on the concentrations of the quenchers. Since β-carotene does not effect any species other than singlet oxygen at such low concentrations ($<10^{-4}$ M),(5) it seems likely that large portions (ca. 80 %) of the photooxygenation proceeds by a non-singlet-oxygen mechanism and that a singlet-oxygen process (ca. 20 %) is operating as a minor competitive process. In the case of azide ion which is known to quench not only singlet oxygen but also triplet state of sensitizers,(7) the value (R_q/R_o) decreases even at higher concentrations of NaN_3.

The product ratio (2/3) determined by VPC at ca. 60 % conversion was strongly dependent on photosensitizer type (Table I). Anthraquinone sulfonate and benzophenone, which are known to be poor sensitizers for singlet-oxygen production but efficient sensitizers for Type I reaction,$^{8)}$ are good sensitizers for the production of benzaldehyde **2**. In addition, the product ratio increases in going from free rose bengal to polymer-bound rose bengal, RB-IRA-400$^{9)}$ or Ⓟ-RB.$^{10)}$ This suggests that polymer-bound sensitizers prefer a Type I reaction over a singlet-oxygen process as compared with the free sensitizers.$^{11)}$ Although polymer-bound sensitizers are widely used for the generation of singlet oxygen in solutions, care has to be taken in using such sensitizers, i.e., polymer-bound sensitizers as well as free sensitizers are capable of undergoing Type I reaction with readily oxidizable substrates like amines or ethers.

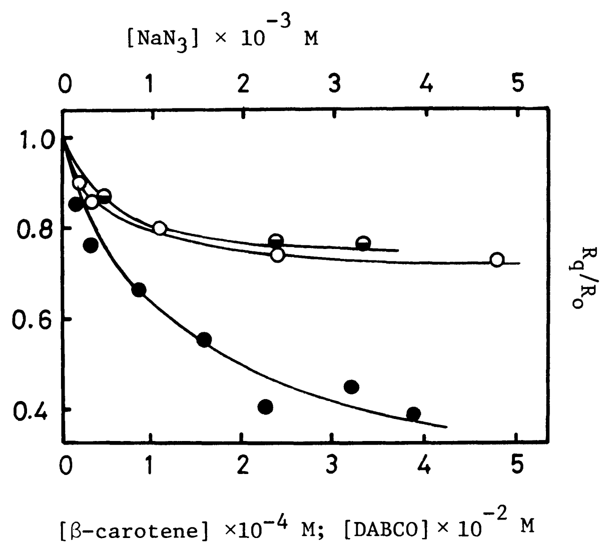

Fig. 1. The inhibitory effect (R_q/R_o) vs. concentrations of singlet-oxygen-quenchers. (◐), β-carotene; (○), DABCO; (●), NaN_3

Table I. Effects of sensitizers on the product ratio (**2**/**3**) in the photooxygenation of **1** (0.01 M)

Sensitizer	Conversion (%)	Yield(mM) **2**	Yield(mM) **3**	Product ratio (**2**/**3**)
Rose bengal^a	67	1.6	0.7	2.3
Methylene blue^a	64	1.3	0.73	1.8
RB-IRA-400^a	65	2.1	0.44	4.8
Ⓟ-RB^a	60	1.8	0.22	8.1
Anthraquinone sulfonate^b	66	3.8	0.11	34.5
Benzophenone^c	61	3.0	0.14	21.6

^{a}In methanol. ^{b}In methanol-benzene (1:2). ^{c}In benzene.

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11) $\Phi_{^1O_2}$ for Ⓟ-RB is reported to be 0.43, whereas $\Phi_{^1O_2}$ for rose bengal in methanol is 0.76.$^{10)}$ This might be one of the reasons for the remarkable difference in efficiency of the processes.

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