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Photooxygenations with Heterogeneous Sensitizers

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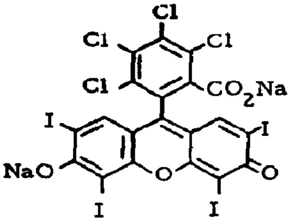
Although many sources of singlet oxygen are now available, the photosensitized formation of singlet oxygen using various dyestuffs remains the method of choice for most synthetic and mechanistic applications. However, there have been several limitations to the photooxidation method: (1) the sensitizer (dye) must be soluble in the reaction solvent limiting the dye/solvent combinations which can be used; (2) the dye is often bleached over long reaction times; (3) the dye can interact with the substrates and/or the products; and (4) the separation of the dye from the products can be difficult.

We have prepared several insoluble polymer-bound dyes and found these heterogeneous sensitizers useful for the photochemical generation of singlet molecular oxygen. Polymer-bound sensitizers have several advantages over the free sensitizers in solution. They can be used in solvents in which the unbound dye is insoluble and therefore unable to sensitize singlet oxygen formation efficiently. They are significantly more stable toward bleaching than are the free sensitizers. The polymer-bound sensitizers can be easily removed at the end of the reaction by filtration, and can be reused with little or no loss in efficiency.



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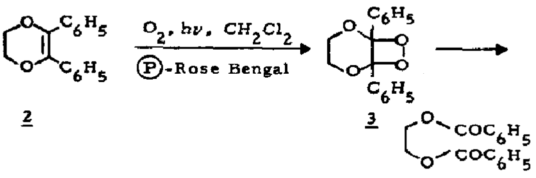
Reaction of Rose Bengal 1 with chloromethylated styrene-divinyl-benzene copolymer beads (200 - 400 mesh, 1.11 meq Cl/g polymer) gave 1 chemically bound to the polymer beads, designated Ⓟ-Rose Bengal. Photooxidation of 2,3-diphenyl-p-dioxene (2) with Ⓟ-Rose Bengal in methylene chloride gave 4 in 95% yield. Absorption spectra of the reaction solution before and after photolysis indicated that no Rose Bengal had leached into the solution during the reaction.



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The results of several control experiments indicate this to be an authentic singlet oxygen reaction sensitized by the *heterogeneous* sensitizer Ⓟ-Rose Bengal. The quantum yield for the production of $^1O_2$ in CH_2Cl_2 with Ⓟ-Rose Bengal is 0.46.

Other sensitizers that have been attached to the polymer beads include eosin-Y, fluorescein, chlorophyllin and hematoporphyrin. Experiments utilizing these Ⓟ-sens will be described.

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The Reactions of Photoexcited SO with Polyunsaturated Olefins

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The reactions of SO_2, photoexcited at 3130A and 25 °C, with C_2H_2 and C_3H_4 (allene) have been studied. With C_2H_2, the sole gas phase product is CO. Its quantum yield, $\Phi\{CO\}$, increases with the ratio $[C_2H_2]/[SO_2]$ to an upper limiting value of 0.04. In the presence of excess CO_2 or H_2O vapor, $\Phi\{CO\}$ is reduced at low values of the ratio $[C_2H_2]/[SO_2]$, but remains unchanged or increases slightly at high values of the ratio. As NO is added it first increases $\Phi\{CO\}$, but then reduces it to zero. The results are consistent with the interpretation that the SO_2 electronic states responsible for the chemistry are the triplet states.