

REACTIONS BY SINGLET OXYGEN AND VIA TRANSIENT COMPLEX
(BETWEEN DYE AND OXYGEN), PRODUCED SIMULTANEOUSLY THROUGH
THE INTERACTION BETWEEN TRIPLET EOSINE AND OXYGEN

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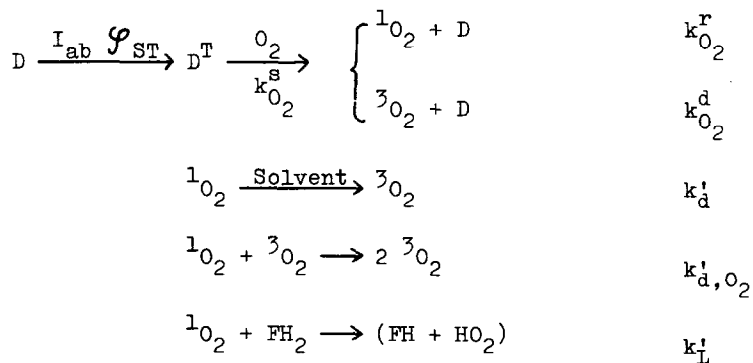
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The photosensitized oxidation of leuco fluorescein (FH₂) in the aqueous solution (pH=6.2) (Reaction I) (1), using eosine (D) and other dyes as a sensitizer, has been studied under such an experimental condition that the initial process is the interaction between triplet dye and oxygen. As an exciting light, only the light longer than the longest wavelength absorption of an each dye was employed using a suitable cut-off filter.

The results obtained, together with the previous results on the photooxidative bleaching of dye (Reaction II) (2)(3) have led us to conclude as follows.

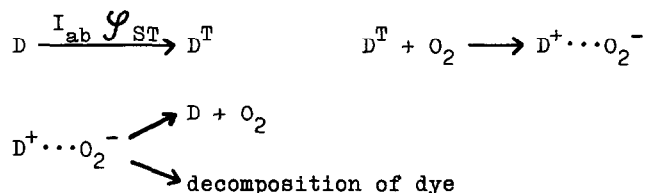
Reaction I occurs via singlet oxygen and according to the following scheme,

Scheme I



Reaction II occurs via complex formation according to the following scheme,

Scheme II



Here $D^+ \cdots O_2^-$ is a complex resembling the ion-pair. Of course most of $D^+ \cdots O_2^-$ reconverts to the original dye and only a little portion decomposes irreversibly (Quantum yield $\sim 10^{-4}$).

The main purpose of the present communication is to present the experimental evidence to substantiate the above two schemes.

Finding 1. The quantum yield for Reaction I, Φ_{D-O} decreases with the increasing oxygen concentration. The rate of Reaction I and hence Φ_{D-O} is given straightforwardly from Scheme I as

$$\Phi_{D-O} = \text{rate}/I_{ab} = \varphi_{ST} \frac{k_{O_2}^r}{k_{O_2}^s} \cdot \frac{k_L^i [FH_2]}{k_d^i + k_{d,O_2}^i [O_2] + k_L^i [FH_2]}$$

Finding 2. The value $k_{d,O_2}^i/k_d^i$ (anticipating Scheme I to hold) was really found to be independent of a sensitizer used; methylene blue, $1.1-1.2 \times 10^{-3} (M^{-1})$; thionine, $1.6-2.2 \times 10^{-3}$; eosine, $1.8-2.5 \times 10^{-3}$ (acridine, 0.6×10^{-3} (1)).

Finding (1) and (2) are in sharp contrast to the kinetic feature of the oxidative photobleaching of dye, where the rate becomes constant beyond a certain small oxygen concentration. Thus for eosine, $\Phi = \sim 3 \times 10^{-4}$ (2) and for methylene blue $\Phi = 0.47 \times 10^{-5}$ (3) irrespective of oxygen concentration in the region from $[O_2] = 2 \times 10^{-5}$ to $3 \times 10^{-4} M$.

The above distinctive difference in the kinetic feature of the two reactions, leads to the following requirement.

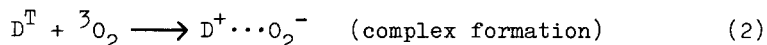
Requirement A. An oxidative species playing an essential role in Reaction I and II must be different.

Furthermore, Finding (2) necessitates the second requirement.

Requirement B. The oxidative species in Reaction I is the same one species

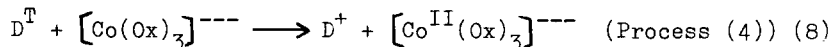
independent of a sensitizer.

Now the following three processes should in general, be taken into account as the possible interaction between triplet dye and oxygen,



The occurrence of Process (1) has been fully established since the appearance of Foote and Wexler's work (4). The occurrence of Process (2) or (3) has been proposed by us (5) on the ground that the transient spectrum due to the half-oxidized eosine is observable in the aerated aqueous solution and Process (2) has been suggested as more likely than (3) because of the first order decay of the species. Process (2) is a special case of the general adduct-theory of Schenck (6). Process (3) was proposed a long time ago by Weiss, Franck, Livingston and others (7). The above three processes can occur in general, simultaneously and the four kinds of transient species, 1O_2 , $D^+ \cdots O_2^-$, D^+ and O_2^- give rise to different types of reaction according to the experimental conditions.

Coming back to the oxidative species involved in Reaction I, only 1O_2 and O_2^- are the ones satisfying Requirement B. In the case of O_2^- however, free D^+ would also be produced at the same time, and the half-oxidized eosine in the free state, which is produced by



has been found to attack very efficiently upon FH_2 . For example, the quantum yield for the system consisting eosine $1 \times 10^{-5}M$, $K_3[Co(Ox)_3]$, $6.0 \times 10^{-4}M$ and FH_2 , $6.0 \times 10^{-5}M$ (pH=6.2) (degassed solution) was ca. 0.15 as compared with 0.006 for Reaction I.

Hence the formation of free O_2^- and accordingly the occurrence of Process (3) is ruled out, and the oxydative species in Reaction I is concluded to be singlet oxygen. It is noteworthy that 1O_2 is deactivated by the ground state

oxygen in the liquid phase.

Turning next to Reaction II, Requirement A in conjunction with the above conclusion, leaves only Process (2) as a possible one. Thus Reaction II is concluded to occur according to Scheme II. This view has been further supported by the following finding and others. The decay of the half-oxidized dye produced in the aerated solution was not affected by the addition of 1×10^{-5} to 2×10^{-4} M of FH_2 , whereas the decay rate of free D^+ produced by Process (4) was very much increased by the addition of FH_2 .

We believe that the present results afford the first chemical evidence for the formation of a rather stable dye-oxygen complex with the nature of ion-pair.

Details will be published elsewhere.

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- (8) to be published. The deaerated aqueous solution of eosine containing $[\text{Co}(\text{Ox})_3]^{---}$, when illuminated, produces a large quantity of half-oxidized dye, which is believed to exist in the free state.