

# Photocatalysis with Xanthene Dyes in Liquid Homogeneous Solutions

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## Abstract

Xanthene dyes (XD) are widely used as photocatalysts in many important organic chemical reactions in the liquid phase. Several such reactions are listed in this brief article. XD react in the excited triplet state  $\text{XD}^*$  of a dye. The reasons for utilizing XD as the redox photocatalysts are explained. A problem is outlined, whether XD act as the photocatalysts or as the reagents partially consumed during a synthesis.

**Keywords:** Photocatalysis; Xanthene dyes; Redox reactions; Oxidation and reduction cycles

## Introduction

Photocatalysis is a rapidly developing area of photochemistry, catalysis, material science. The appearance of a new Journal of Photocatalysis testifies to this fact. Photocatalysis is homo- or heterogeneous catalysis by molecules [radicals] in the electronically excited singlet or triplet states [excited doublet or quartet states]. There are several recent review articles devoted to photocatalysis [1-3]. This brief review article is devoted to photocatalysis with xanthene dyes (XD) in homogeneous liquid solutions. These and some other dyes proved to be effective photocatalysts of diverse liquid-phase chemical reactions, see below. A mechanism of action of XD is our main focus. The structures of XD are presented below. See scheme 1. Scheme 1 does not exhaust all the known XD. XD is used also as mono- or di-substituted, either sodium carboxylates or sodium carboxylates and sodium alkoxides. Some XD structures have a methyl or an ethyl substituent. It is necessary to refer to the original publications for details.

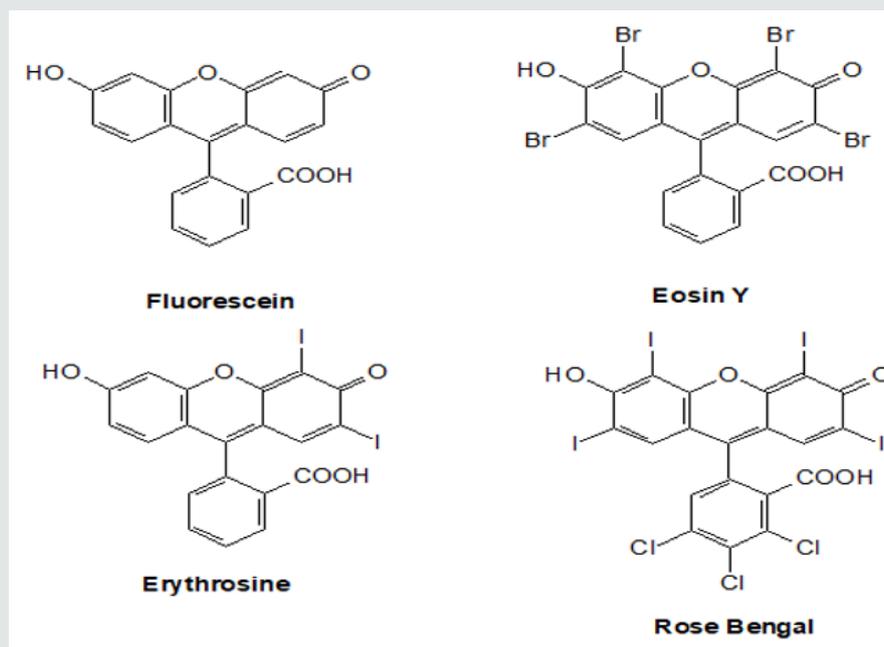
## Photoreactions of Xanthene Dyes

Absorption of visible light leads to the formation of an excited singlet state of  $^1\text{XD}^*$  with a subsequent intersystem crossing into a reactive triplet state  $^3\text{XD}^*$ . We will note parenthetically that XD

(Scheme 1) is the classical example of an internal heavy atom effect: introduction of halogen atoms into the Fluorescein moiety leads to an increase of quantum yield of a triplet state. XD reacts in the excited triplet state [4]. We will denote that state as  $\text{XD}^*$ . The use of XD as photocatalysts is based on the change of redox properties of XD under photoexcitation. XD become “more powerful” oxidants and “more powerful” reductants in the excited state compared to the same properties in the ground state.  $\text{XD}^*$  easily oxidize donors (D) in the solution like amines and  $\text{XD}^*$  are oxidized by acceptors (A) like nitrobenzene. Such reactions do not proceed with non-photo excited XD. Table 1 below presents approximate values of the redox potentials of XD and their derivatives for a semi-quantitative comparison of potentials.

**Table 1:** Approximate Values of Redox Potentials of XD,  $\text{XD}^*$  and Their Radical-Cations and Radical-Anions<sup>a</sup>.

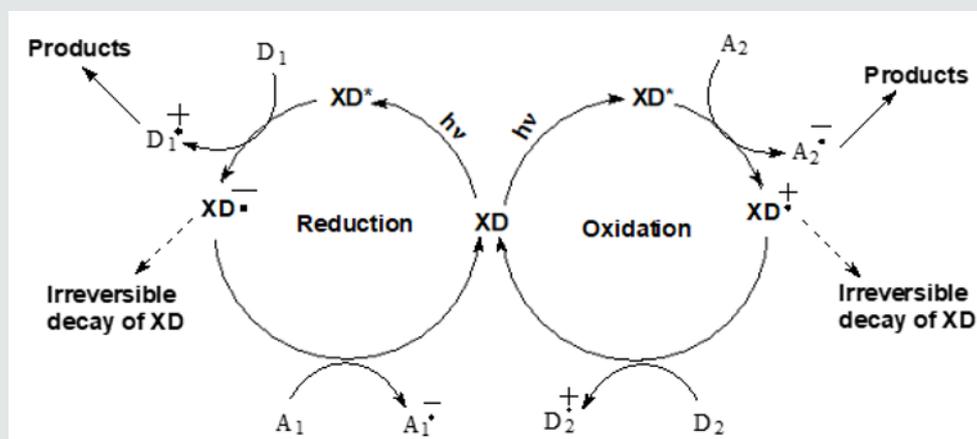
Redox Couple	Redox Potential, V
$\text{XD}^+/\text{XD}^*$	-1.1
$\text{XD}^+/\text{XD}$	0.8
$\text{XD}^*/\text{XD}^-$	1
$\text{XD}/\text{XD}^-$	-1



**Scheme 1:** Chemical structures of the xanthene dyes (XD).

<sup>a</sup>Potentials vs. saturated calomel electrode (SCE). Solvent – acetonitrile. Data of ref. [2,3,5,6]. See the original publications for the precise data. The principle of action of XD as photocatalysts is presented in Scheme 2 below. XD\* produces charged (Scheme 2) or neutral radicals of a substrate. These radicals participate in further reactions leading to the organic products of interest.  $A_{1(2)}$  stands for an electron acceptor;  $D_{1(2)}$  stands for an electron/hydrogen donor. We present elementary reactions of XD\* as a single electron transfer (SET) [5].  $A_2^-(D_1^+)$  can react with  $H^+$  (can release  $H^+$ ) and form a neutral radical, see Scheme 2. Alternatively, the reaction of XD\* may be an H- abstraction with a charge-transfer transition state.  $D_1^+$  and  $A_2^-$  (Scheme 2) form the intermediate radical products. These intermediate products eventually lead to the product of interest after two or more reactions with available reagents. One

of the intermediate products of XD\* reactions can serve as  $A_1$  or  $D_2$ , see Scheme 2.  $A_1$  has often considered dioxygen is the air-saturated solutions, see e.g. [3,10]. We will mention some of such important for organic chemistry reactions photo catalyzed by XD: bromination, hydroxylation, arylation of heteroarenes, cyclization of thioamides, arylation of bezothiophenes, borylation of aryl diazonium salts, dehydrogenative coupling and cross-coupling, coupling of substituted tetrahydroisoquinoline with nitromethane, reduction of nitrobenzene in the presence of amine, desulfurization, the formation of iminium ions, photopolymerization in the presence of amine and photoinduced electron/energy transfer–reversible addition–fragmentation chain transfer (PET-RAFT) polymerization [2,3,5, 7-12]. See for details the cited literature and references cited therein.



**Scheme 2:** Generalized presentation of a reductive and of an oxidative cycle with the participation of xanthene dyes (XD). Two circles represent two different reactions.

## Photocatalysis or photoinduced reactions?

The original publications on photocatalysis with XD usually present oxidative or reductive cycles like it is depicted in Scheme 2. Reactions leading to **Products** (Scheme 2) are also identified [2,3,5,7-12]. It is stated that reactions with XD are photocatalysis. Strictly speaking, a photocatalyst should not be consumed in the course of a photocatalytic reaction. However, some publications indicate consumption of XD in the course of its action as a "photocatalyst" [8,11]. In the cases of consumption of XD one can talk on the "visible light-mediated" photoreactions [11] or light promoted reactions [10], or the photoinduced reactions. New products obtained with the help of XD\* are mostly interesting for organic chemistry and not a fate of XD. It would be interesting to know the results of a simple experiment: take Vis spectra of solutions of XD prior to and after the ending of a reaction [13]. (Essential changes of [XD], which are probably due to bleaching, can be noticed by a naked eye in a glass vessel.) We presented with dashed lines possible and even probable irreversible decay of XD in the course of its action, see Scheme 2. Usually irreversible decay of XD is not reflected at a nice circle in publications.

A concentration of XD in such photocatalytic reactions is different. XD use in a concentration of  $1 \cdot 10^{-5}$  M [8,11], 1-2 mol% [3,5]. Sometimes higher [XD] is desirable up to 5 ml% [10]. (Unfortunately, we have different units of concentration.) Initial  $[O_2]$  in the air-saturated solutions is  $\sim 10^{-3}$  M [6]. It is not obvious that  $A_1 = O_2$  effectively regenerates XD during the whole process (Scheme 2).

The matter is not only of using strict terminology. (Photo) chemistry of dyes is a valuable area of chemistry, and side reactions of XD maybe of importance. Some publications pay attention to quenching of XD\* by dioxygen in the air-saturated solutions with a formation of singlet dioxygen in the course of photocatalysis [3].  $^1O_2$  is not an inert species and it can participate in different reactions [3]. In general, it is not surprising that the yield of the final product of interest catalyzed by XD is less than 100% like it often happens in the dark synthesis.

## Conclusions

It is possible nominally call XD participating in reactions cited above as photocatalysts. XD is relatively inexpensive. They

succeeded in many processes expensive photocatalysts - complexes of "heavy atoms" (Ir, Ru) [2]. XD are excited with visible light, and the modern LED light sources can be utilized. XD as photocatalysts meet the demand for green chemistry.

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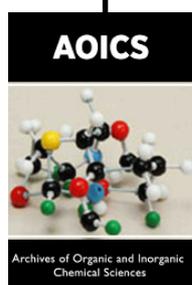
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