

Photoinduced electron transfer in the ion pair compound (XTO_n): influence of ionic association

Wenhui Zhou *, Erjian Wang

Institute of Photographic Chemistry, Academia Sinica, Beijing 100101, People's Republic of China

Received 30 January 1995; accepted 1 November 1995

Abstract

The influence of the ionic dissociation equilibrium on the photochemical and photophysical properties of xanthene dye onium salts (XTO_n) was studied. The dissociation constants (K_D) determined by conductivity verify that the ionic association states directly influence the changes in the absorption spectral shape, and the ratio I_{532}/I_{445} reflects the degree of dissociation of the system. The results of static fluorescence quenching and dynamic lifetime quenching experiments demonstrate that the electron transfer of XTO_n is mainly intra-ion pair electron transfer; the quenching rate constants of intra-ion pair electron transfer approach 10^{12} – 10^{13} s⁻¹ M⁻¹, which is well above the rate limit controlled by diffusion. The effects of substituents and solvents show that the process of electron transfer is controlled by the degree of association, and the efficiency of photosensitized initiation may be improved further by a shift in the equilibrium.

Keywords: Association state; Ion pair; Electron transfer; Iodonium salt

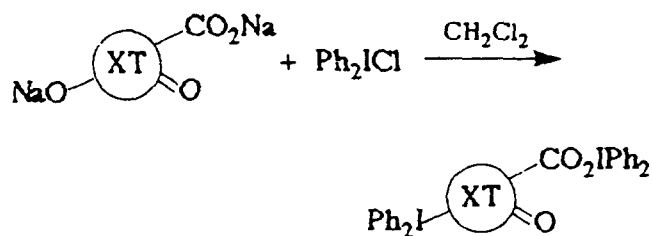
1. Introduction

The development of new advanced materials for laser and photocuring requires the investigation of novel photosensitization systems which respond to visible and IR light [1–4]. Dyes with a photoresponse covering the entire visible and near-IR region are abundant, and are important photosensitizers. Aromatic onium salts (On) are cation and radical initiators [5,6], but they absorb below 300 nm which severely limits their applicability in photopolymerization. Fortunately, iodonium salts possess low reduction potentials and are easily photosensitized by electron transfer reaction. Usually, the photosensitized reaction involves bimolecular electron transfer or energy transfer [7,8]; the reaction is controlled by diffusion so that, in solid and viscous media with low molecular mobility, it cannot occur effectively within the short lifetime of the excited state. In order to avoid this problem, the photosensitizer and initiation component are pre-assembled by various bond links. The method in which the two components are bonded through electrostatic interaction between anions and cations is convenient and effective. Zhou et al. [9] have reported a novel photosensitized initiation system of eosin bis(diphenyliodonium) salt (EON). On exposure to visible light, this system rapidly undergoes intra-ion pair electron transfer to form the reactive radical, which

then initiates the polymerization of unsaturated monomers. A modified system containing various xanthene dyes to increase the range of the spectral response has been reported [10]. We have synthesized a series of xanthene dye iodonium salts. We report the influence of the ionic dissociation equilibrium on the photochemical and photophysical properties of these salts and discuss the process of electron transfer and its controlling factors.

2. Experimental details

Six xanthene dye iodonium salts (XTO_n) were synthesized by ionic exchange between xanthene dye and diphenyliodonium chloride



where XT ≡ fluorescein (FL), 4,7-dichlorofluorescein (FC), 4,7-diiodofluorescein (FI), eosin (EO), erythrosin (ER) and rose bengal (RB).

* Corresponding author.

Table 1
Thermodynamic parameters of photosensitization system XTON

XTON	E_S (kcal mol ⁻¹)	E_T (kcal mol ⁻¹)	E_{ox} (V)	E_{red} (V)	ΔG_S (kcal mol ⁻¹)	ΔG_T (kcal mol ⁻¹)
FL	55.86	44.7	0.91	-1.13	-30.3	-19.1
FC	54.58	44.7	0.95	-1.07	-28.1	-18.2
FI	55.64	44.0	0.88	-1.18	-30.7	-19.1
EO	53.16	44.0	0.80	-1.04	-30.1	-20.1
ER	52.77	44.8	0.79	-1.09	-29.9	-22.0
RB	50.0	41.8	0.88	-0.95	-25.1	-16.5

Eosin ethyl ester idonium salt (EOEtOn) was obtained by esterification of the C-2' carboxyl group of eosin and ionic exchange according to the above step.

Acetonitrile (AN) of analytical purity was used after distillation; 1,4-dioxan was used after refluxing with sodium for 16 h followed by distillation; the other agents of analytical purity were used as received.

The dissociation constant (K_D) of EOEtOn was determined by measuring the conductivity on a DDS-12 conductivity gauge in solutions of different concentration at 25 °C. Using the equation $1/\lambda_m = 1/\lambda_m^\infty + \lambda_m \times c / (K_D \lambda_m^\infty)$, where λ_m and λ_m^∞ are the molar and limiting molar conductivity respectively, K_D was obtained from the slope and section of the plot of $1/\lambda_m$ vs. $\lambda_m c$.

The photobleaching light source was a xenon lamp (light below 300 nm filtered out with hard glass) and the intensity of irradiation was 2.45 mW cm⁻². The photobleaching rate was expressed by the relative change in the maximum optical density of the absorption peak at long wavelength as a function of the irradiation time

$$R_b = (OD_0 - OD) / OD_0 t$$

The quantum yields (Φ) were calculated according to

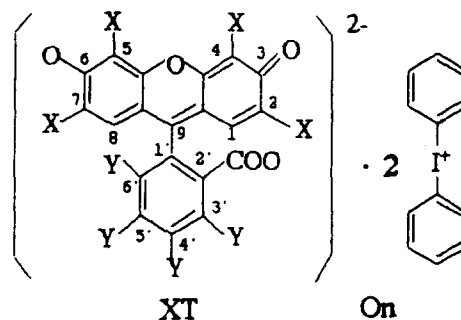
$$\Phi = R_r / 2.303 I_0 \epsilon b c$$

where R_r is the rate of the photoreaction and I_0 is the intensity of irradiation.

The lifetime and fluorescence quenching experiments were conducted on an NEAS HORIBA-NAES-100 time-resolved spectrofluorometer and a Hitachi MPF-4 fluorescence spectrophotometer, and the absorption spectra were recorded on a Hitachi 557 UV-visible spectrophotometer.

3. Results and discussion

The structures of the various xanthene dye idonium salts (XTON) synthesized are shown below.



XT	X	Y	λ_{max} (nm)	ϵ_{max} (M ⁻¹ cm ⁻¹)
FL	4H	4H	500	0.47
FC	2H, 2Cl	4H	508	1.03
FI	2H, 2I	4H	517	1.72
EO	4Br	4H	528	8.45
ER	4I	4H	531	7.90
RB	4I	4Cl	561	8.52

The free energy of electron transfer (ΔG_{et}) can be used to determine whether or not a reaction will occur and reflects the driving force for the reaction. On the basis of the Rehm-Weller equation (according to the redox potentials of the xanthene dyes and idonium salt and the energies of the excited singlet and triplet states of the dyes), the values of ΔG_{et} were calculated. From Table 1, it can be seen that the values of electron transfer (ΔG_{et}) between xanthenes and idonium salts are negative on exposure to light. Theoretically, this indicates that photoreaction may occur from the singlet and triplet states of the dye and a high driving force is observed.

3.1. Association states and absorption spectral properties

XTON salts are a type of organic ionic compound which may exist as a mixture of three ionic association states: freely solvated ions, ion pairs and aggregates. The concentration of our system is very low (approximately 10⁻⁵ M), so that aggregates are not observed; therefore an equilibrium between free ions and ion pairs exists. According to the Fuoss equation

$$K_D = [3000 / (4Na^3)] \times \exp\{-[e^2 / (a\epsilon k_b T)]\} \quad (1)$$

the dissociation constant (K_D) depends on the dielectric constant of the solvent (ϵ), the centre to centre distance for contact of the ions in the ion pairs (a) and the temperature of the solution (T). Moreover, for the large sizes of these ionic compounds, the dissolvability of the medium will significantly influence the ionic association states.

In ordinary conditions, the spectral properties of solvent-separated ion pairs (loose ion pairs) and free ions are very similar; however, the shape and peak position of the absorption spectrum of tight ion pairs are different from those of solvent-separated ion pairs and the absorption is usually blue shifted. The reason for this is that the distance between the anion and cation in the tight ion pair is so short that their electronic clouds can interact with each other [11]. In dioxan-AN, we have studied the effect of solvent polarity on the absorption spectrum (Fig. 1). It can be seen that, in the polar solvent AN, EON exhibits one set of long-wavelength absorption peaks (set I: 532, 500 nm); following an increase in the dioxan content, i.e. decreasing solvent polarity, the peaks at long wavelength gradually decrease, and a new set of absorption peaks at short wavelength (set II: 445, 380 nm) appears.

The set of peaks at long wavelength can be attributed to the characteristic peaks of freely solvated ions and the other

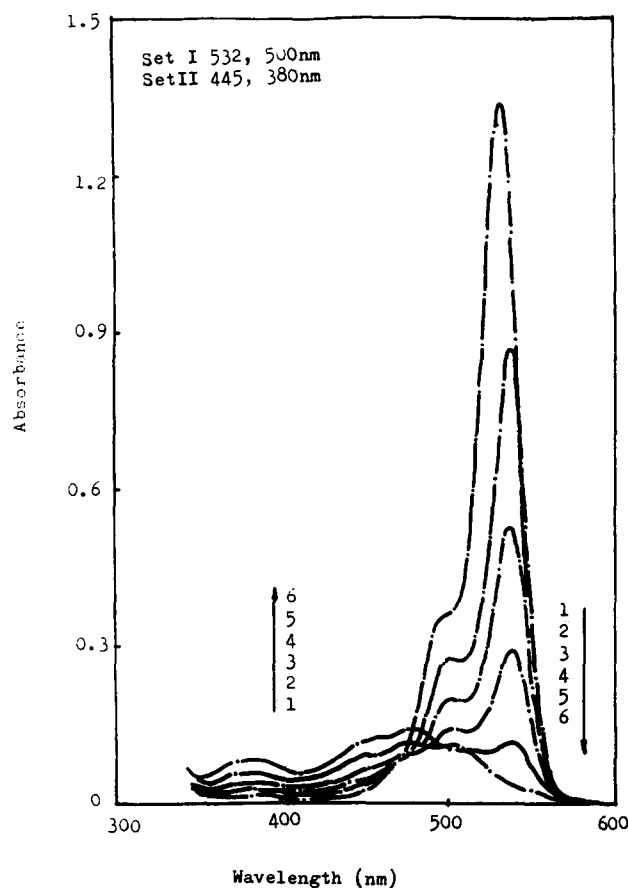


Fig. 1. Effect of solvent polarity on the spectrum of eosin iodonium salt in AN-1,4-dioxan. 1,4-Dioxan (vol.%): 1, 0; 2, 20; 3, 40; 4, 60; 5, 80; 6, 100; concentration of EON, $2 \times 10^{-5} \text{ mol l}^{-1}$.

Table 2

Dissociation constant and I_{532}/I_{445} ratio of EOEtOn in a mixture of AN and dioxan

Parameter	An (vol.%)					
	0	20	40	60	80	100
I_{532}/I_{445}	0.2	1.0	3.0	5.5	9.0	
$\lambda_m^\infty \times 10^2 \text{ (sm}^2 \text{ mol}^{-1}\text{)}$	0.0	0.28	1.22	1.39	1.52	2.23
$K_D \times 10^5$	0	0.45	0.91	4.22	5.68	9.83

set can be assigned to ion pairs. An increase in solvent polarity causes an increase in the degree of dissociation and a proportional enhancement of the I_{532}/I_{445} ratio. Therefore this ratio can be used to evaluate the degree of dissociation of the system.

In order to confirm the relationship between the degree of dissociation of XTON and the I_{532}/I_{445} ratio, the dissociation constants (K_D) were obtained by the conductivity method. Because XTON is a binary salt, it is difficult to measure the dissociation constants K_{D1} and K_{D2} . Fortunately, the plane of the 2'-carboxylphenyl group is perpendicular to that of the xanthene moiety of the dyes and the absorption characteristics of the molecule in the visible region depend mainly on the association states of the 4-phenoxy group [12]. Therefore eosin ethyl ester monoiodonium salt (EOEtOn), instead of EON, was chosen for measurement of the conductivity of solutions of different concentration and solvent polarity. The conductivity of EOEtOn at a concentration of $4.0 \times 10^{-4} \text{ M}$ in dioxan is zero on the smallest scale ($0-0.2 \text{ scm}^{-1}$) of the conductivity gauge, indicating that the ions of EOEtOn predominantly exist as ion pairs. With an increase in the proportion of AN, the limiting molar conductivity (λ_m^∞) and K_D values increase. It is clear that the changes in K_D are consistent with those of the I_{532}/I_{445} ratio (Table 2). The value of K_D is 9.83×10^{-5} in AN and, if the concentration is 10^{-5} M , 91.5% of the salt will dissociate into free ions in this polar solvent.

3.2. Studies of the fluorescence quenching by onium salts

The quenching of the fluorescence intensity and lifetime was carried out at room temperature. Dynamic quenching of the lifetime usually involves a bimolecular collision process which is controlled by diffusion. The lifetime obtained for eosin anions is 2.21 ns in AN, similar to the reported value [13]. The rate constants of lifetime quenching obtained from a Stern-Volmer plot for a 9:1 mixture of dioxan and AN are close to the corresponding values of static quenching ($10^{13} \text{ M}^{-1} \text{ s}^{-1}$). Because, in non-polar solvents, the K_D value of EON is zero, the cations and anions rapidly associate into ion pairs; since this process is controlled by a strong static electroforce and not by molecular diffusion, it is impossible to observe the pure quenching reaction of freely solvated ions. However, in polar solvents, most of the salt (more than 90%) exists as free ions; the quenching of the lifetime involves a

collision process between free cations and anions, and therefore the quenching rate constant ($6.27 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) is controlled by diffusion and is much lower than that of static fluorescence quenching (Table 3). Although the proportion of free ions is much higher than that of ion pairs in AN, the static quenching rate constant shows that the reaction of ion pairs plays an important role. Overall, the reaction rate constants depend on the proportion of ion pairs in the solvent. The higher the proportion of ion pairs, the more rapid the electron transfer. Therefore it is expected that the rate of electron transfer of XTON can be controlled by changing the ionic association states.

3.3. Studies of the photobleaching reaction

On irradiation with visible light, electron transfer occurs between excited xanthene dyes and iodonium salts (Scheme 1) to form radical pairs ($\text{XT}^{\cdot}/\text{On}^{\cdot}$) which may undergo back electron transfer to regenerate the initial ion pair or carbon-iodine bond cleavage to form neutral iodobenzene (PhI) and the phenyl radical (Ph^{\cdot}) in a solvent cage with XT^{\cdot} . Ph^{\cdot} can also undergo back electron transfer with XT^{\cdot} to return to the ground state, couple and disproportionate with XT^{\cdot} to generate the leuco form of the dye or diffuse from the solvent cage to generate the free radical which undergoes further secondary reaction or may be applied to initiate polymerization of a monomer. During the photoreaction, the bleaching of the dye causes changes in the absorption spectrum which can be used to monitor kinetically the process of electron transfer.

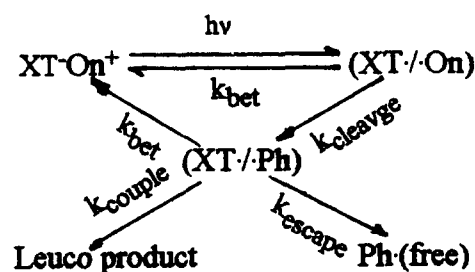
3.3.1. Effect of substitution

The minimum energy structure of EOOon has been studied using the computer molecular modelling technique [12], and it has been demonstrated that the onium cation may be bonded to phenoxy and carboxyl anions in different configurations. The intra-ion pair electron transfer will firstly occur on the phenoxy anion bonded to the xanthene moiety. The photobleaching data of various xanthene dyes are outlined in Table 4. On the whole, we can see that the bleaching rates (R_b) and quantum yields (Φ_r) are in the order $\text{FL} > \text{FC} > \text{EI} > \text{EO} > \text{ER} > \text{RB}$. Obviously, the halogen atom substituents in the skeleton of the xanthene moiety, especially in the ortho positions of the phenoxy group, will play an important role in electron transfer. The higher the electrophilic effect of the halogen atoms ($\text{Cl} > \text{Br} > \text{I} > \text{H}$), the lower the electron cloud density on the phenoxy anion, and thus the electrostatic attraction of the phenoxy anion to the iodonium cation grad-

Table 3
Quenching rate constants of eosin with onium in mixtures of AN–dioxan

Rate constant	10	50	100
$k_q (\text{M}^{-1} \text{ s}^{-1})$	3.75×10^{13}	7.52×10^{12}	2.91×10^{12}
$k_q (\text{M}^{-1} \text{ s}^{-1})$	3.45×10^{13}		6.27×10^{10}

k_q, k_q , fluorescence quenching rate constants of intensity and lifetime.



Scheme 1. Process of intra-ion pair electron transfer of XTON.

Table 4
Photobleaching of various xanthene iodonium salts

	FL	FC	FI	EO	ER	RB
I_t/I_{11}	2.04	2.57	2.80	8.41	7.86	10.70
$R_b \times 10^2 \text{ s}^{-1}$	4.20	2.91	2.48	3.59	1.85	1.93
Φ_r	0.33	0.29	0.18	0.12	0.09	0.03

[XTON] = $2 \times 10^{-5} \text{ mol l}^{-1}$ in CH_2Cl_2 in the presence of nitrogen.

Table 5
Absorption and photobleaching data of EOOon in EAc–AN mixtures

EAc (%)	Dielectric constant	λ_{max} (nm)	$\epsilon_{\text{max}} \times 10^{-4}$ ($\text{cm}^{-1} \text{ M}^{-1}$)	I_t/I_{11}	$R_b \times 10^2$ (s^{-1})	Φ_r
0	37.5	532	4.99		0.24	0.050
20	30.1	533	3.82	10.1	2.65	0.076
40	22.7	535	2.91	9.23	4.31	0.083
60	15.4	537	1.85	8.75	5.56	0.102
80	7.98	539	1.43	8.51	8.13	0.124
100	6.02	540	1.20	8.24	9.24	0.152

Concentration, $2 \times 10^{-5} \text{ l}^{-1}$ in the presence of nitrogen.

ually decreases from FL to RB. In addition, the steric hindrance, depending on the size of the halogen substituent ($\text{I} > \text{Br} > \text{Cl} > \text{H}$), increases the distance between cation and anion. The above two factors may decrease the degree of orbital overlap and weaken the interaction between donor and acceptor. As a result, xanthene dyes with halogen atom substituents easily form freely solvated ions and their degrees of dissociation (I_t/I_{11}) increase from FL to RB, similar to the order of the photobleaching rates. These results indicate that the rate of electron transfer changes in an opposite manner to the pure degree of dissociation of XTON. Overall, the negative effect of the substituent, depending on the electric properties and steric hindrance, is in the order $\text{I} > \text{Br} > \text{Cl} > \text{H}$.

3.3.2. Effect of solvent polarity

As mentioned above, the polarity and dissolvability of the solvent directly affect the degree of dissociation of the XTON salt, and have an important influence on the photoreaction. The photobleaching data of EOOon in solvents with different proportions of AN and ethyl acetate (EAc) are outlined in Table 5. Because of the changes in the extinction coefficient of the absorption peak at long wavelength in the different mixtures, the quantum yields are used as a reasonable criterion for comparison. It is clear that, following the increase in

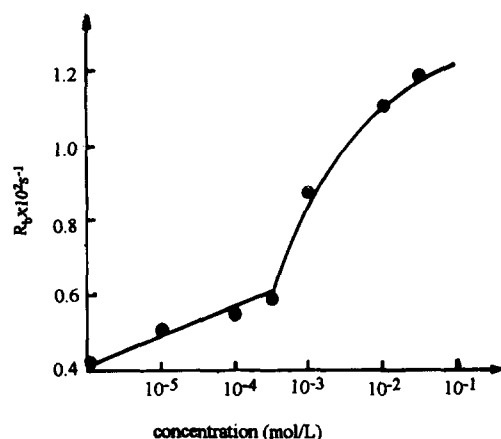


Fig. 2. Effect of addition of onium on the photobleaching of RBO in AN; $[\text{RBO}] = 2 \times 10^{-5} \text{ mol l}^{-1}$ in the presence of nitrogen.

EAc content, the degree of dissociation (I_I/I_{II}) of EOO gradually decreases, but the quantum yield of reaction increases strongly. This result is consistent with fluorescence quenching data.

3.3.3. Effect of salt addition

The low solubilities of XTON salts in non-polar solvents severely limits their applicability to the photopolymerization of monomers. Although XTON salts are soluble in polar solvents, their dissociation results in a decrease in the rate and quantum yield of initiation. In addition, polymerization reactions are usually disturbed by impurities and oxygen, especially for those xanthene dyes having higher Φ_{isc} values such as ER and RB. Fortunately, the addition of onium to the system helps to move the equilibrium towards the formation of ion pairs. Of the xanthene dyes, RB has the highest Φ_{isc} value (approximately unity); the effect of addition of an onium salt on the rate and efficiency of electron transfer is especially significant to this system (Fig. 2). When the initial concentration of onium salt is lower than $5 \times 10^{-4} \text{ M}$, the photobleaching rate increases slowly and exhibits an almost linear relationship to the concentration of onium. However, when the concentration reaches $5 \times 10^{-4} \text{ M}$ or more, the bleaching rate increases sharply and finally attains a constant value. This indicates that RBO mainly exists as free ions in the initial state, with the addition of a low concentration of onium, and only a few ion pairs are formed. As more salt is added, the proportion of intra-ion pairs increases. When the concentration of onium is in the range 10^{-3} – 10^{-2} M , the effect is remarkable.

4. Conclusions

XTON salts naturally exist as freely solvated ions and ion pairs, their proportion depending on the structure of the xanthene dye and the polarity of the solvent. During photoreaction, they may undergo rapid intra-ion pair electron transfer ($k_{et} = 10^{12}$ – $10^{13} \text{ M}^{-1} \text{ s}^{-1}$); the proportion of ion pairs has an important influence on the rate of electron transfer. The unstable radicals produced by electron transfer rapidly undergo bond cleavage to form active fragments of the preliminary radical. This type of rapid consecutive reaction helps to decrease back electron transfer and inactivation in the solvent cage and enhances the reaction efficiency of the radical formed.

Acknowledgements

We thank the National Science Foundation of China for financial support; this work was reported at the Third Japan–Sino Binational Symposium on Photochemistry, Osaka, October, 1994.

References

- [1] J.H. He and E.J. Wang, *Acta Polym. Sinica*, 5 (1992) 664.
- [2] M. Kawabata, M. Harada and Y. Takimoto, *J. Photopolym. Sci. Technol.*, 1 (1988) 222.
- [3] D.C. Neckers, *J. Photochem. Photobiol. A: Chem.*, 47 (1989) 1.
- [4] S. Chatterjee, P. Gottschalk, P.P. Pavis and G.B. Shuster, *J. Am. Chem. Soc.*, 110 (1988) 2326.
- [5] R.S. Davison and J.W. Goodwin, *Euro. Polym. J.*, 18 (1982) 589.
- [6] H. Banmann, B. Strehmel and H.J. Timpe, *Euro. Polym. J.*, 22 (1986) 313.
- [7] J.P. Foussier, P.J. Longnot, A. Paverner and F. Wider, *Chem. Phys. Lett.*, 135 (1987) 30.
- [8] R.S. Davison and J.W. Goodwin, *Euro. Polym. J.*, 18 (1982) 597.
- [9] W.H. Zhou, J.H. He, M.Z. Li and E.J. Wang, *Photogr. Sci. Photochem.*, 13 (1995) 103.
- [10] W.H. Zhou, M.Z. Li and E.J. Wang, *J. Photopolym. Sci. Technol.*, 1 (1994) 241.
- [11] C. Reichart, *Solvents and Solvent Effects in Organic Chemistry*, 2nd edn., VCH, Weinheim, 1988, p. 359.
- [12] J.H. He, W.H. Zhou and E.J. Wang, *Acta Chem. Sinica*, in press.
- [13] P. Bilski, R. Dabestani and C.F. Chignell, *J. Phys. Chem.*, 95 (1991) 5784.