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Photoinduced Electron and H-atom Transfer Reactions of Xanthone by Laser Flash Photolysis†

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The property of the lowest excited triplet states of xanthone in acetonitrile was investigated using time-resolved laser flash photolysis at 355 nm. The transient absorption spectra and the quenching rate constants (k_q) of the excited xanthone with several amines were determined. Good correlation between $\lg k_q$ and the driving force of the reactions suggests the electron transfer mechanism, except aniline and 3-nitroaniline (3-NO$_2$-A) which showed energy transfer mechanism. With the appearance of ketyl radical, hydrogen atom transfer also happened between xanthone and dimethyl-*p*-toluidine, 3,5,N,N-tetramethylaniline, N,N-dimethylaniline, and triethylamine. Therefore, both electron transfer and H-atom transfer occured in these systems. Great discrepancies of k_q values were discovered in H-atom abstraction reactions for alcohols and phenols, which can be explained by different abstraction mechanisms. The quenching rate constants between xanthone and alcohols correlate well with the α-C$-$H bonding energy of alcohols.

Key words: Laser flash photolysis, Xanthone, Electron transfer, H-atom transfer

I. INTRODUCTION

Electron transfer and hydrogen atom transfer reactions are important processes in both chemistry and biochemistry. Bimolecular electron transfer reactions between photoexcited aromatic ketone, quinones and amines have been investigated using laser flash photolysis [1-4]. The hydrogen atom transfer reactions of carbonyl compounds with a variety of substrates such as alcohols, hydrocarbons and amines are also well-known [5-8].

The photochemistry of xanthone (XT) has been well studied and we know the lowest triplet energy changes in character from π, π^* in polar solvents to n, π^* in non-polar solvents [5]. The variation in XT triplet $\lambda_{\max}$ has already been used as a sensor of environmental polarity [9-11]. Ketones having low lying π, π^* triplets are known to be substantially less reactive in hydrogen abstraction than those having low lying n, π^* states [12]. Despite the lower reactivity toward H-atom abstraction for the lowest triplet π, π^* of XT in acetonitrile, its reactivity somewhat increases when the $^3(\pi, \pi^*)$ state is mixed with a close-lying $^3(n, \pi^*)$ state by vibronic interaction [5]. The triplet state and ketyl radical of XT have also been characterized by laser flash photolysis [5-7,13,14].

Although XT is a well studied and frequently employed sensitizer, there are few investigations with regard to the quenching processes by a series of amines and alcohols, especially to giving an explanation of the

reaction mechanism.

In this work, laser flash photolysis studies of XT with a series of amines and alcohols to determine the mechanisms of observed photoinduced electron and hydrogen transfer reactions are presented. The quenching rate constants of XT by a number of amines and alcohols are reported and the authors speculate on the mechanism of the reactions through the changes of transient absorption spectra. Negative driving force (ΔG) values suggest that the proposed electron transfer step is thermodynamically feasible. Furthermore, a plot of the $\lg k_q$ of electron transfer *vs.* ΔG is presented in the light of Rehm-Weller theory.

II. EXPERIMENTS

3,5,N,N-tetramethylaniline (TMA), triphenylamine (TPA), dimethyl-p-toluidine (DMT) were obtained from Fluka and were used without further purification. XT and phenol were recrystallized from ethanol twice. N,N-dimethylaniline (DMA), triethylamine (TEA), and phenethyl alcohol were distilled twice before being used. 1,3-dihydroxybenzene and 1,4-dihydroxybenzene were recrystallized from toluene twice. Benzyl alcohol, methanol, ethanol, 1-propanol, 2-propanol, aniline (AN), and 3-nitroaniline (3-NO$_2$-A) were used directly without further purification. The acetonitrile used as a solvent was spectrophotometric grade. The resulting solutions were bubbled with high-purity argon (99.99%) for 20 min before the spectroscopic measurements. All the spectra were recorded at ambient temperature.

The third harmonic (355 nm) of a Q-switched Nd:YAG laser (Spectra Physics, GCR-170, repetition rate of 10 Hz) with a duration of 8 ns was used as an excitation source in the laser flash photolysis experiments
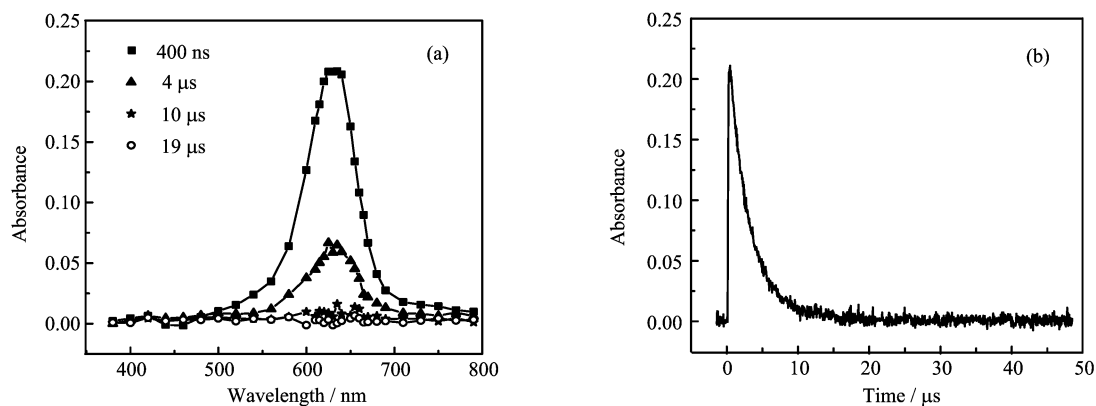

395

FIG. 1 (a) Transient absorption spectra observed in the laser flash photolysis of XT (0.5 mmol/L) after 355 nm laser pulse in Ar-saturaterd acetonitrile. (b) Decay time profile of 630 nm in Ar-saturated solutions.

as described previously [3,15]. The analyzing light was from a 500 W Xenon lamp. The laser and analyzing light beams passed perpendicularly through a quartz cell with an optical path length of 10 mm. A monochromator (MC-30N, Ritsu Oyo Kogaku Co.Ltd.) equipped with a GDB 59 photomultiplier at the rear of the exit slit was used to analyze the absorption. The signals from the photomultiplier were displayed and recorded as a function of time on a Tektronix TDS 380 oscilloscope. Each datum was determined by a 256-time average to improve the signal-to-noise ratio. To avoid errors due to the accumulation of products, the samples were often irradiated in a flow cell attached to a reservoir where the stock solution was deaerated. The transient absorption spectra were obtained from a series of oscilloscope traces measured with the stock solution of flow cell in a point-by-point manner with respect to the wavelength.

III. RESULTS AND DISCUSSION

A. Transient absorption spectra and self-quenching of $^3XT^*$

Photoexcitation of XT solutions in deaerated acetonitrile with a 8-ns laser pulse at 355 nm generates broad absorption spectra with maxima at 630 nm (Fig.1(a)). This is attributed to laser-produced triplets of XT, which is consistent with earlier reports [5,6]. The signal decay can be fitted with first-order kinetics at low excitation doses (with energy of 5 mJ), as shown in Fig.1(b).

The first-order rates observed at low excitation energy are concentration dependent, reflecting self-quenching of the triplet. Therefore we used a relatively low concentration of XT (5×10^{-4} mol/dm^3) in the spectra of XT with a series of quenchers.

Figure 2 shows the plots of the first-order rates (k_0) for the decay of $^3XT^*$ as function of XT in acetonitrile. From the straight line, the k_0 can be expressed as

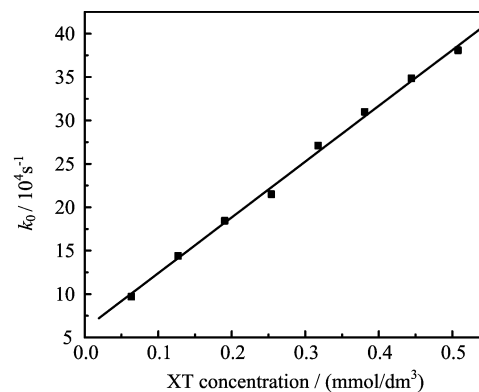

FIG. 2 Quenching rate constants for XT triplets as a function of the concentration of XT in acetonitrile.

Eq.(1),

$$k_0 = 1/\tau_0 + k_{sq}[XT] \tag{1}$$

where k_{sq} is the self quenching rate constant of XT and τ_0 is the lifetime of the triplet. From the intercept and slope of the straight line, the value of k_{sq} and τ_0 were determined as 6.45×10^8 L/(mol s) and 16.8 μs, respectively, under these experiment conditions. It has also been reported that the values of k_{sq} and τ_0 were 4.5×10^8 L/mol s and 8.3 μs in acetonitrile contained 0.04% water [5]. Repeating those experiments in the current study produced similar results of $k_{sq}=4.0\times10^8$ L/(mol s) and $\tau_0=9.7$ μs. These results shows marked solvent dependence.

B. Bimolecular rate constants measurement

In photoinduced reactions the strongly active nature of the XT triplet makes it easy to abstract electron and hydrogen from different quenchers, so the experiments were carried out with XT and a variety of quenchers in acetonitrile. Quenching experiments were

chosen at the band of 630 nm. Bimolecular quenching rate constants for the reactions of $^3XT^*$ with a variety of donors were obtained by plotting the observed rate constants(k_{obs}) versus the quenchers, concentration according to Eq.(2).

$$k_{obs} = k_0 + k_q[\text{quencher}] \qquad (2)$$

where k_0 and k_q denote the decay rate of the triplet state in the absence and presence of quencher, respectively. The quenching rate constants including electron transfer and H-atom reactions are listed in Table I and II.

TABLE I Quenching rate constants for the triplets of XT by different quenchers in acetonitrile, oxidation potentials (E_{ox}) *vs* SCE of quenchers in acetonitrile, free energy changes (ΔG) for electron transfer of XT with amines in acetonitrile

Quencher	$k_q/(10^{10}$ L/mol s)	E_{ox}/V *vs.* SCE	$\Delta G/eV$
DMT	0.625	0.7 [16]	−0.808
TMA	1.203	0.74 [4]	−0.768
DMA	1.185	0.81 [18]	−0.698
TPA	0.5747	0.85 [19]	−0.658
TEA	0.237	0.96 [20]	−0.548
AN	1.125	0.98 [17]	−0.528
3-NO$_2$-A	1.17	1.28 [17]	−0.228

TABLE II Quenching rate constants for the triplets of XT by different hydrogen donors in acetonitrile

Quencher	$k_q/(\text{L/mol s})$	Bonding energy of C−H/(kJ/mol)
Methanol	2.01524×10^5	401.85 [22]
Ethanol	4.368×10^5	396.8 [23]
1-propanol	4.67696×10^5	390.1 [24]
2-propanol	6.77334×10^5	380.9 [21]
Phenethyl alcohol	2.85576×10^7	369.6 [24]
Benzyl alcohol	9.68222×10^7	366.2 [24]
Phenol	2.13466×10^9	
1,3-dihydroxybenzene	4.74679×10^9	
1,4-dihydroxybenzene	7.6507×10^9	

C. Electron transfer and hydrogen transfer reactions with amines

Evidence for the electron transfer and hydrogen transfer mechanisms was obtained from the time-resolved transient spectra containing XT and a series of amines in acetonitrile. On laser flash photolysis of XT in the presence of TPA which can not donate hydrogen, three transient absorption bands located at 370, 550, and 650 nm are formed, as shown in Fig.3. Due to the absorption bands overlap of XT triplet maxima at 630 nm and TPA radical cation maxima at 650 nm, it was decided to select the transient absorption of a long
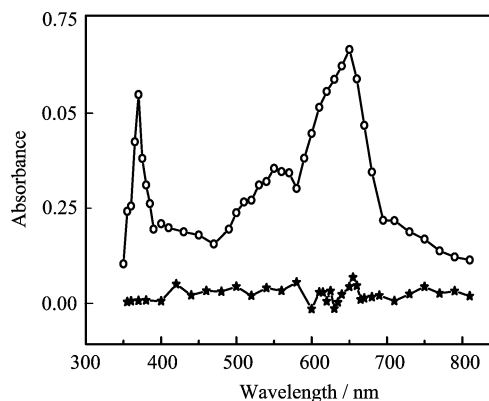

FIG. 3 Transient absorption spectra observed in the laser flash photolysis of pure XT (0.5 mmol/L) (⋆) and XT (0.5 mmol/L) with TPA added (0.193 mmol/L) (○) 19 μs after 355 nm laser pulse in Ar-saturated acetonitrile.

decayed time (19 μs) after 355 nm laser pulse when the absorption of pure XT triplet is almost zero. The contrast of the absorption spectra between pure XT and XT with TPA added is shown in Fig.3. In Fig.3, the three peaks due to the addition of TPA can be seen clearly. These three peaks are assigned to the absorption of TPA radical cation, which is supported by previous work [25]. The absorption of XT radical anion can be considered as the background of all the spectrum due to its weak absorption in the band of 350-700 nm [26,27]. These observations suggest that the reaction pathway involves electron transfer.

Laser flash photolysis was also employed on other three aniline derivatives (DMT, TMA, DMA) with similar configurations. Figure 4(a) shows the transient spectra obtained from XT/DMT in Ar-saturated acetonitrile. After the laser pulse, a new peak with maximum at 480 nm was detected along with the fast decay of $^3XT^*$. This long-lived transient absorption at 480 nm was attributed to the radical cation of DMT [4]. Similar behaviors were also seen with quenchers TMA and DMA (Fig.4 (b) and (c)). Two new peaks at 500 and 475 nm were ascribed to the radical cations of TMA and DMA respectively, while the transient absorption peaks of TMA and DMA radical cations were at 510 and 465 nm in acetonitrile [4]. The reason for the ascription of TMA and DMA radical cation is shown below.

Moreover, a similarity can be found in Fig.4, namely the common absorption peak at 380 nm. In order to clarify this absorption peak, an experiment of transient absorption spectrum of XT and phenol was carried out. Generally speaking, since electron transfer reaction cannot occur between phenol and ketone, the absorption peak in the spectrum was considered as the result of hydrogen abstraction. As shown in Fig.5, the transient absorption spectrum of XT/phenol was obtained using laser flash photolysis in which the absorption peak of 380 and 480 nm appeared. Inasmuch as the absorption of phenoxy radical is negligibly small [8], the absorp-
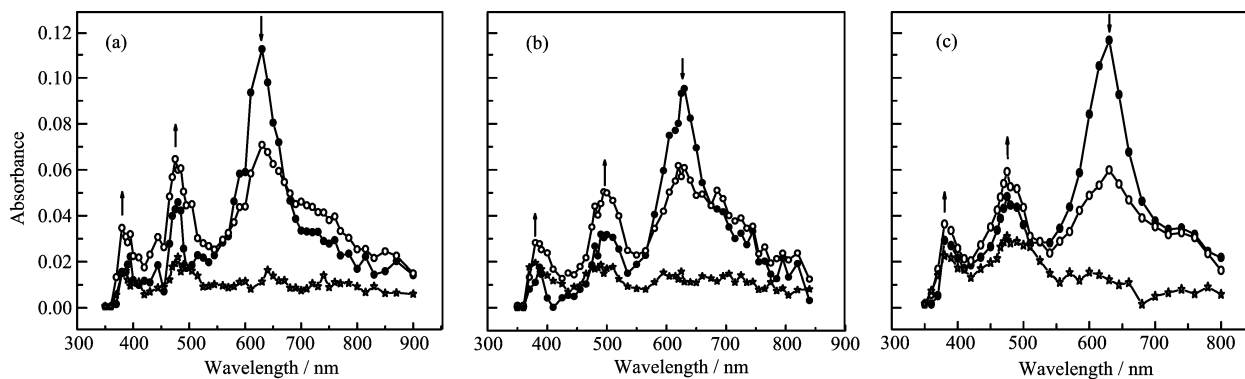

FIG. 4 Transient absorption spectra observed in the laser flash photolysis of XT (0.5 mmol/L) with (a) DMT (0.1 mmol/L) 0.42 μs (●), 0.72 μs (○), 19 μs (⋆) (b) TMA (0.1 mmol/L) 0.4 μs (●), 0.7 μs (○), 19 μs (⋆), and (c) DMA (0.18 mmol/L) 0.5 μs (●), 1 μs (○), 19.4 μs (⋆) after 355 nm laser pulse in Ar-saturated acetonitrile.
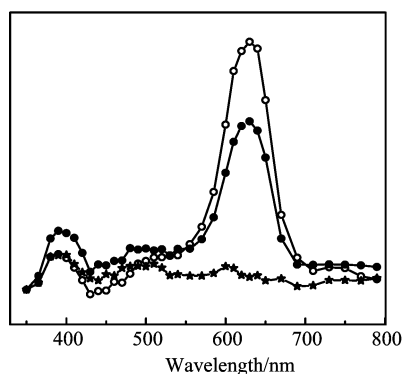

FIG. 5 Transient absorption spectra observed in the laser flash photolysis of XT (0.5 mmol/L) with phenol (3.4 mmol/L) 0.4 μs (○), 0.7 μs (●), 19.4 μs (⋆) after 355 nm laser pulse in Ar-saturated acetonitrile.

Scheme 1

tion peak of 380 and 480 nm can be attributed to the XT ketyl radical. This assignment is also in accordance with previous research [7,28].

Therefore, the difference of the absorption peaks of TMA and DMA radical cation between these results and the literature values can be explained by the coexistence of electron transfer and hydrogen transfer. In this work, the transient absorption spectra at 500 nm in XT/TMA is the overlap of the absorption spectra of TMA radical cation at 510 nm and XT ketyl radical at 480 nm, and the absorption of 475 nm is the overlap of XT ketyl radical at 480 nm and DMA radical cation at 465 nm. In the transient absorption spectra of XT/DMT, due to the identical absorption peaks of the XT ketyl radical and DMT radical cation, the absorption peak at 480 nm is the superposition of the two radicals. From above discussion, we can conclude that both electron transfer and hydrogen transfer processes exist in these photoinduced reactions. The mechanism of photoinduced electron transfer and hydrogen transfer reactions is depicted in Scheme 1.

Furthermore, electron transfer and hydrogen transfer
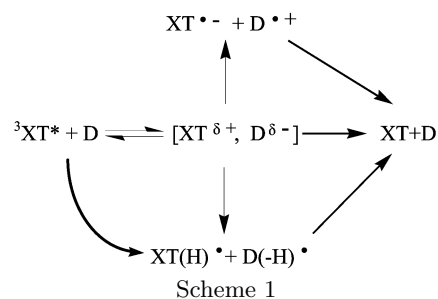
reaction can also occur in the photoinduced reaction of XT/TEA. The quenching rate constants of XT/amines including hydrogen and electron transfer reactions are listed in Table I. Since >99% of the quenching rate constants can be attributed to electron transfer, and hydrogen transfer can only contribute a little to the quenching rate constants, so k_q indicates the property of the electron transfer [6]. There is a good correlation between lgk_q and the oxidation potential (E_{ox}) of the amines in Table I. With the increasing of the E_{ox}, the k_q reduced except AN and 3-NO$_2$-A which increased abnormally. We can attribute the abnormal increase of k_q to the occurrence of energy transfer, because of their lower triplet energy than XT [29,30].

To further prove the thermodynamic feasibility, an effort was made to determine the rate constants in quenching reactions as a function of the free energy change ΔG (Table I), which could be calculated by the Rehm-Weller [32] equation:

$$\Delta G = E_{ox} - E_{red} - q^2/\varepsilon r - E_T \qquad (3)$$

where E_{ox} (in V) and E_{red} (in V) are the oxidation potential of the donor and the reduction potential of the acceptor, respectively. E_T (in eV) is the excited state energy of the sensitizer. For XT the value of E_{red} is -1.76 V (*vs.* SCE) in acetonitrile [6]. $q^2/\varepsilon r$ is the work term which accounts for the coulombic energy of the product ions at the encounter distance ($q^2/\varepsilon r$=55 meV in acetonitrile). E_T has been estimated to be around
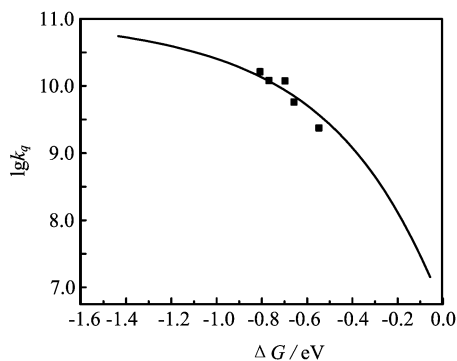

FIG. 6 Plot of $\lg k_q$ vs. ΔG for photoinduced thermal electron transfer reactions of XT.

309.8 kJ/mol [31]. As shown in Fig.6, the plot of $\lg k_q$ vs. ΔG reveals a typical dependence of the quenching rate constants of electron transfer reactions on the free energy change of the reactions.

The dependence of k_q on $\Delta G^{\neq}$ for electron-transfer quenching is calculated according to the following equation using the steady state approximation:

$$k_q = \frac{k_d}{1 + 0.25[\exp(\Delta G/RT) + \exp(\Delta G^{\neq}/RT)]} \quad (4)$$

where k is the Boltzmann constant and k_d is the rate constant of diffusion of the encounter complex. Here, it is taken as 2×10^{10} L/mol s which is obtained from the Debye expression [34]. $\Delta G^{\neq}$ is the free energy of activation for electron transfer. The dependence of $\Delta G^{\neq}$ and ΔG has already been established by Rehm-Weller relationships [32].

$$\Delta G^{\neq} = \frac{\Delta G}{2} + \left[\left(\frac{\Delta G}{2}\right)^2 + (\Delta G_0^{\neq})^2\right]^{1/2} \quad (5)$$

The unexplained term in the above expression is $\Delta G_0^{\neq}$, which is nothing but the free energy of activation when there is no driving force for the reaction, i.e. $\Delta G^{\neq} = \Delta G_0^{\neq}$ at $\Delta G = 0$. For the present investigation, the $\Delta G_0^{\neq}$ value is obtained via the conventional way of plotting $\Delta G^{\neq}$ vs. ΔG and is 28.9 kJ/mol (0.3 eV).

As can be seen from Table I, when $\Delta G < -66.4$ kJ/mol (0.698 eV), the electron transfer quenching rate constant approaches the diffusion-controlled limit and almost remains constant at 2×10^{10} L/mol s. In Fig.6, the plot of $\log k_q$ vs. ΔG correlates well with the solid line derived from Rehm-Weller relationship [32], and also exhibits a typical feature of the photoinduced electron transfer process.
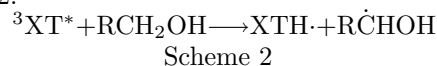
D. Hydrogen abstraction with alcohol and hydroxybenzene

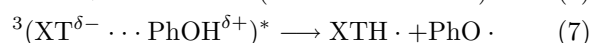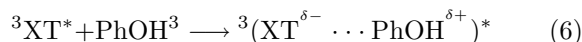Hydrogen abstraction in the triplet states of aromatic ketones and quinones is one of the most thor-

oughly studied photochemical reactions [8]. Experiments of XT/2-propanol and XT/benzyl alcohol were carried out, producing the results shown in Fig.7. Transient absorption peaks of 380 and 480 nm, which are similar to those of Fig.5, were found in the two spectra. In the foregoing discussions, the absorption peaks of 380 and 480 nm were ascribed to the XT ketyl radical. So we can conclude that hydrogen transfer has happened between XT and 2-propanol, benzyl alcohol.

In these experiments, a variety of typical hydrogen donors, such as aliphatic alcohol, benzyl alcohol and hydroxybenzene, were also used to quench the triplet of XT at the band of 630 nm. The quenching rate constants were listed in Table II.

As can be seen from Table II, there is a fairly good correlation between quenching rate constants (k_q) and the bonding energy of the α-C−H of alcohol. These observations suggest that the dominant reaction pathway is one that involves hydrogen abstraction from the C−H to the carbonyl of XT. The relevant process is shown in Scheme 2.

$$^3XT^* + RCH_2OH \longrightarrow XTH\cdot + R\dot{C}HOH$$
Scheme 2

Phenolic hydrogen abstraction is known to be faster than benzylic and alcoholic hydrogen abstraction [8]. That was confirmed in these experiments when H-atom donors were replaced by phenol and diphenols with the quenching rate constant changing by a factor of 2-4. This great discrepancy comes from the different hydrogen abstraction mechanisms. In an XT/alcohol system, a direct hydrogen abstraction from aliphatic hydrocarbon takes place. As for the XT/phenol system, the triplet excited complexes with charge transfer character would be produced via the collision process between $^3XT^*$ and PhOH. The protic H atom of PhOH is ready to transfer to carbonyl groups of XT due to the coulombic interaction in the triplet exciplexes with charge transfer character, resulting in an XTH radical and the corresponding phenoxy radical. Namely, the former is an H-atom abstraction from hydrocarbon, while the latter is a protic H-atom transfer reaction from phenols [8]. It was also found that the more protic the H atom is, the more reactive it is in the hydrogen transfer, which is in accordance with previous research [8]. The possible mechanism may be as follows:

$$^3XT^* + PhOH^3 \longrightarrow {}^3(XT^{\delta-} \cdots PhOH^{\delta+})^* \quad (6)$$
$$^3(XT^{\delta-} \cdots PhOH^{\delta+})^* \longrightarrow XTH\cdot + PhO\cdot \quad (7)$$
Scheme 3

IV. CONCLUSION

The triplet state of XT in acetonitrile was generated and studied by laser flash photolysis. Aniline derivatives were found to quench triplets of XT markedly. Quenching rate constants (k_q) varied with free energy change, which was in accordance with the electron
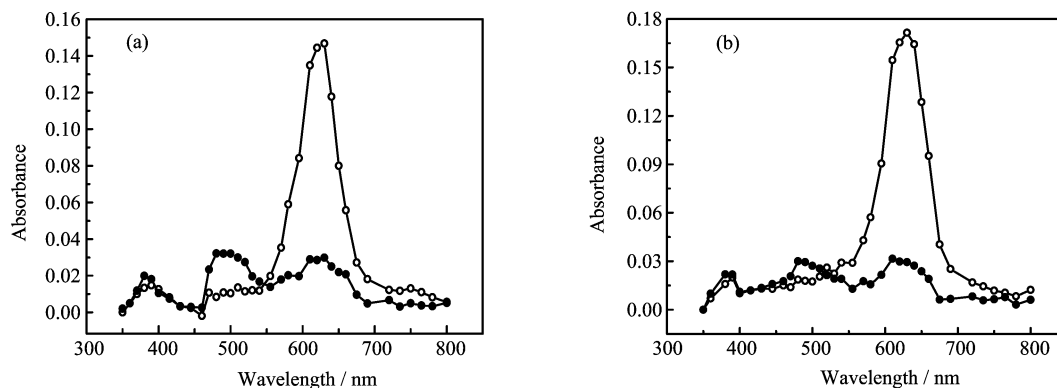

FIG. 7 Transient absorption spectra observed in the laser flash photolysis of XT (0.5 mmol/L) with (a) 2-propanol (5.23 mol/L) 0.44 μs (○), 2 μs (●) and (b) benzyl alcohol (65 mmol/L) 0.4 μs (○), 2 μs (●) after 355 nm laser pulse in Ar-saturated acetonitrile.

transfer mechanism, except AN and 3-NO$_2$-A which were presented by an energy transfer mechanism. With the appearance of the ketyl radical, the reaction pathway of DMT, TMA, DMA, TEA with XT is electron transfer and H-atom transfer. Alcohols and hydroxybenzenes were also found to quench triplets of XT through the mechanism of hydrogen abstraction.

V. ACKNOWLEDGMENT

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