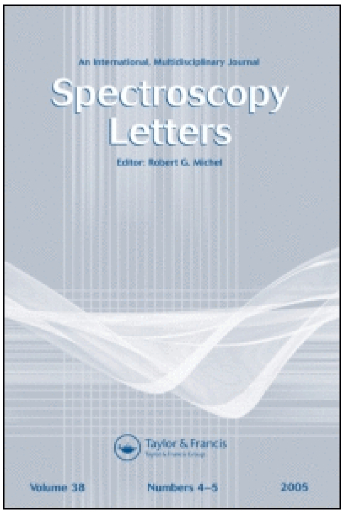

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Viscosity Effect Study on Quenching of Photoinduced Excited Triplet Duroquinone by TEMPO

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ABSTRACT Quenching dynamics of excited quinone molecules are given much attention in photochemistry and biochemistry. In order to study the viscosity effect on the quenching of triplet excited state of duroquinone (^{3}DQ*) by stable radical, 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO), this study measured chemically induced dynamic electron polarization (CIDEP) spectra and transient absorptive spectra in various solvents. The solvents used were ethylene glycol, 1,2-propanol and their mixtures with different ratio in volume. The Stern-Volmer plot was obtained form CIDEP spectra of photolysis of DQ with different TEMPO concentrations. Combining the slope of the Stern-Volmer plot with lifetime of ^{3}DQ*, determined from the ^{3}DQ* transient absorbance decay curve, the quenching rate constants of ^{3}DQ* by TEMPO were calculated in each solvent. The results indicate that the quenching rate constant is viscosity-dependent, and that it decreases linearly with the increase in solvent viscosity in the range used in our experiment.

KEYWORDS exited triplet duroquinone, TR-ESR, transient absorptive spectrum, viscosity effect

1. INTRODUCTION

Quinone compounds are widely distributed in biological systems and play important roles in photosynthesis and aerobic respiration.[1] Triplet excited states of quinines can be generated by UV light irradiation in human skin and in plant leaves or by non-photochemically enzymatic and nonenzymatic redox cycling.[2] These triplet quinones may cause damage in biological systems either directly by electron transfer or hydrogen transfer reaction or indirectly by acting as singlet oxygen sensitizers.[3–6] Since triplet quinones can damage biological cells and tissues, investigations on the photochemical reaction of quinones and the quenching of triplet quinones have been of great interest for several decades.[7–10]

Duroquinone (DQ) is a representative aromatic quinone. The lifetime of excited singlet duroquinone (^{1}DQ*) is only 12 picoseconds, and the intersystem crossing (ISC) coefficient is 0.91[8], so the excited triplet duroquinone (^{3}DQ*) can be formed easily in photochemical and biological processes.

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The reduction potential of ${}^3DQ^*/DQ^{-\cdot}$ couple is about 2.17 V and the lowest triplet is $n\pi^*$, so ${}^3DQ^*$ is a relatively powerful one-electron oxidant and hydrogen acceptor.[7] Recently, T. Tachikawa et al. reported the photoinduced electron transfer reaction between ${}^3DQ^*$ and erythrosin B.[11] Bisby et al. reported hydrogen atom transfer from 6-palmitoyl–L-ascorbic acid ($PASCH_2$) and vitamin E to ${}^3DQ^*$, respectively.[8] In our recent work, we observed the hydrogen atom transfer from ethylene glycol (EG) to ${}^3DQ^*$ and the spin polarization on stable radical 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO) when it was added into DQ/EG solution.[12]

Quenching of excited molecules with free radicals is an interesting subject of photochemistry. As far as ${}^3DQ^*$ is concerned, the reported quenching dynamics investigation mainly focus on the electron donor quenchers.[13] Quenching dynamics of ${}^3DQ^*$ by a stable radical, such as TEMPO, has not been reported until now. Moreover, it is well known that micelle may have great influence on the photochemical reaction mechanism and dynamics. Photochemical mechanism of ${}^3DQ^*$ in aqueous SDS micelle and TX-100 micelle microenvironment have been reported.[8,14] Furthermore, solvent viscosity is also an important fact to influence the photochemical reaction mechanism and dynamics of excited triplet molecules.[15–17] Solvent viscosity can affect the tumbling motion of excited triplet molecules effectively in solution, so the spin-lattice relaxation time and diffusion coefficient of the excited triplet will be affected resultantly.[18]

Since viscosity of solvent influences the reaction dynamics of excited triplet molecules, we believe that the viscosity of solvents should have a significant effect on the quenching rate of TEMPO to ${}^3DQ^*$. We know time-resolved electron spin resonance (TR-ESR) technique and transient absorptive spectrum are powerful tools for investigating photoinduced chemical intermediates. TR-ESR technique, especially, can help us observe the chemically induced dynamic electron polarization (CIDEP) phenomenon.[19–21] CIDEP signal can provide much information about photochemical reaction mechanisms and reaction dynamics between triplet excited states and their quenchers, as well as the interaction between the radicals generated subsequently.[9,10,15,16] In the present work, with EG, 1,2-propanol (PG), and their mixtures with different ratios in volume as solvents and TEMPO as quencher, the CIDEP spectrum and transient absorptive spectrum of photolysis of DQ/EG and DQ/TEMPO are measured to investigate the viscosity effect on the quenching of ${}^3DQ^*$ by TEMPO.

2. EXPERIMENTAL

The photolysis experiment was performed on home-made submicrosecond time-resolved ESR spectrometer without field modulation, which has been described in detail elsewhere.[22] The instrument consists mainly of a conventional X-band ESR spectrometer, an boxcar integrator (Stanford SR 252), a digital oscilloscope (Philips PM 3350), and a broadband preamplifier with 50 ns time response. A K-129 klystron is used as microwave source. The microwave system adopts uses a balanced reflection bridge-type circuit and a zero-difference beat balanced frequency-mixing model. The sample cavity is a TE102 rectangular cavity with a high unloaded Q value of approximately 2000. The output of the balanced frequency mixer is transmitted to the broadband preamplifier and then to the digital oscilloscope, or to the boxcar integrator. Third harmonic generation light (355 nm, 15 mJ) from a Nd: YAG laser (Continuum Surelite11–10) operating at the repetition of 10 Hz was used for photoexcitation. The gate width of the boxcar was 0.3 μs. The sample solutions were deoxygenated by bubbling with N_2. To avoid overheating, the solutions were made to flow through a quartz flat cell (optical path: 0.3 mm) in the EPR cavity.

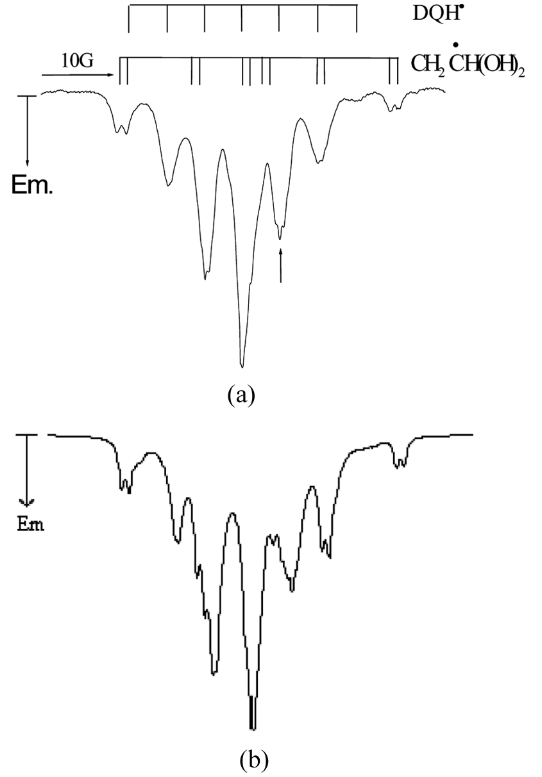
The transient absorptive spectrum was acquired on the transient absorptive spectrum setup at University of Science and Technology of China.

Ethylene glycol and 1,2-propanol were of an A.R. grade. DQ was carefully purified by sublimation under vacuum circumstance. TEMPO was commercially available (Acros Organics, Geel Belgium) and used as received. The concentration of DQ was $15\,\mathrm{m\,mol\,L^{-1}}$.

3. RESULTS AND DISCUSSION

3.1. CIDEP Spectra and Dynamics of Photolysis of DQ/TEMPO in EG

We have reported the CIDEP spectrum of photolysis of DQ in EG with 286 nm dye laser.[12] The CIDEP spectrum obtained in photolysis of DQ/EG solution



(a)

(b)

FIGURE 1 (a) Experimental CIDEP spectrum of photolysis of DQ in EG at room temperature. The Boxcar gate was opened at 0.8 (μs after laser irradiation. (b) Simulated CIDEP spectrum of DQH˙ and $CH_2\dot{C}H(OH)_2$ with the parameters mentioned in the text.

at 0.8 s after 355 nm Nd: YAG laser excitation was shown as Fig. 1(a). The CIDEP signal can be divided into two groups (as shown by the stick spectrum). One is the six double lines with $g = 2.0030$ and hyperfine coupling constants $a_{H(\alpha)} = 17.5G$, $a_{2H(\beta,CH2)} = 9.9G$, $a_{H(\beta,OH)} = 1G$, which can be assigned to EG ketyl radical $CH_2\dot{C}H(OH)_2$.[23] The other is the seven broad hyperfine lines with $g = 2.0048$ and hyperfine coupling constant $a_{H(o,CH3)} = 4.9G$, which can be assigned to neutral durosemiquinone radical DQH˙.[24] There is smaller, unresolved hyperfine splitting on the CIDEP spectra of $CH_2\dot{C}H(OH)_2$ and DQH˙ because of the limited spectrometer resolution. These radicals may be produced by a hydrogen transfer from solvent EG to the excited triplet state $^3DQ^*$. Furthermore, it can be seen that the spectrum is in total emission, which indicates that the polarization is generated mainly by the triplet mechanism (TM). Fig. 1(b) is the simulated CIDEP spectrum of DQH˙ and $\dot{C}_2H_3(OH)_2$ according to the g factor and hyperfine coupling constants mentioned above. The consistency between the simulation spectrum and the experimental one means the assignment for the CIDEP signal and the analysis to polarization mechanism are reasonable. So the possible photophysical and photochemical process during the photolysis of DQ in EG may be as follows

$$DQ \xrightarrow{h\nu} {}^1DQ^* \xrightarrow{ISC} {}^3DQ^* \tag{1}$$

$$^3DQ^* \xrightarrow{^3T_1^{-1}} DQ \tag{2}$$

$$^3DQ^* + CH_2CH_2(OH)_2 \xrightarrow{k_r} DQH^{\cdot} + CH_2\dot{C}H(OH)_2 \tag{3}$$

Equation (1) indicates that the ground state of DQ reaches its single excited state $^1DQ^*$ after absorbing a photon and the triplet excited state $^3DQ^*$ is then formed through ISC. Equation (2) indicates that the relaxation of $^3DQ^*$ and $^3T_1$ $^3T_{-1}$ is the spin-lattice relaxation time. Equation (3) indicates that $^3DQ^*$ captures a hydrogen from EG and then polarized DQH˙ and $CH_2\dot{C}H(OH)_2$ radicals are generated. During the hydrogen transfer reaction, the polarization on $^3DQ^*$ transfers to DQH˙ and $CH_2\dot{C}H(OH)_2$ with the total as a constant. k_r is the reaction rate constant of $^3DQ^*$ with EG.

It is well known that a triplet excited state can interact with a stable radical after laser irradiation in solution.[15,25–28] When TEMPO is added into DQ/EG solution, the CIDEP spectrum obtained was shown as Fig. 2. In addition to the CIDEP signal of DQH˙ and $CH_2\dot{C}H(OH)_2$, there are three new hyperfine lines in Fig. 2 (shown as the stick spectrum) and the hyperfine coupling constant is 16 G. These three new hyperfine lines can be assigned to polarized TEMPO, which always can be seen in the photolysis of other photosensitive molecules/TEMPO

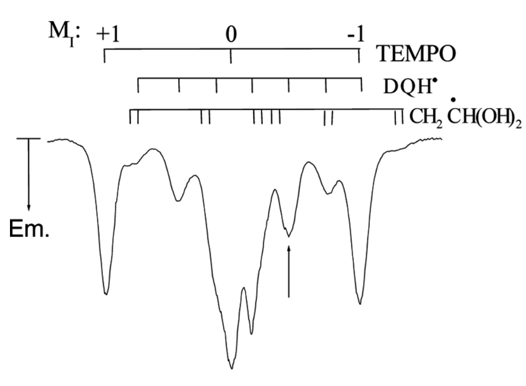


FIGURE 2 CIDEP spectrum of photolysis of DQ/TEMPO in EG at room temperature. The Boxcar gate was opened at 0.8 (μs after laser irradiation. The TEMPO concentration is 2 mmol/L^{-1}.

system.[27] The existence of $DQH^{\cdot}$ and $CH_2\dot{C}H(OH)_2$ in Fig. 2 indicates that there is still a hydrogen transfer reaction form EG to $^3DQ^*$, and the emissive pattern means the main polarization mechanism is still the TM. As for the emissive CIDEP signal on TEMPO, it can be interpreted as the result of the interaction between $^3DQ^*$ and TEMPO, that is, the quartet precursor radical triplet pair mechanism (RTPM). So, we can see that $^3DQ^*$ is quenched not only chemically by EG but also physically by TEMPO during the photolysis of DQ/EG/TEMPO solution. The quenching process of $^3DQ^*$ by TEMPO can be shown as Eq. (4).

$$^3DQ^* + TEMPO \xrightarrow{k_q} DQ + TEMPO^* \tag{4}$$

where, k_q is the quenching rate constant of $^3DQ^*$ by TEMPO.

We know the CIDEP signal of duroquinone radical anion ($DQ^{\cdot -}$) is composed of 13 sharp hyperfine lines with hyperfine coupling constant 1.9 G due to equivalent coupling to 12 protons.[29,30] However, $DQ^{\cdot -}$ is not observed here, indicates that there is not a electron transfer reaction from TEMPO to $^3DQ^*$.

Furthermore, it can be seen that the CIDEP signal of $DQH^{\cdot}$ and $CH_2\dot{C}H(OH)_2$ in Fig. 2 are much weaker than that in Fig. 1(a). The signal of $CH_2\dot{C}H(OH)_2$ is so small that it is not well resolved, perhaps because the quenching of TEMPO to $^3DQ^*$ decreases the probability of hydrogen transfer between $^3DQ^*$ and EG. As far as the quenching of $^3DQ^*$ is concerned, there is a competition between EG and TEMPO.

On the assumption that the rate constant of generation of $^3DQ^*$ after laser excitation is I, the following dynamic Eq. (5) ~ (8) can be obtained according to above photophysical and photochemical reactions.

$$\frac{d[^3DQ^*]_0}{dt} = I - {}^3T_1^{-1}[^3DQ^*]_0 - k_r[^3DQ^*]_0 \tag{5}$$

$$\frac{d[DQH^{\cdot}]_0}{dt} = k_r[^3DQ^*]_0 \tag{6}$$

$$\begin{aligned}\frac{d[^3DQ^*]}{dt} &= I - {}^3T_1^{-1}[^3DQ^*] - k_r[^3DQ^*] \\ &\quad - k_q[TEMPO][^3DQ^*]\end{aligned} \tag{7}$$

$$\frac{d[DQH^{\cdot}]}{dt} = k_r[^3DQ^*] \tag{8}$$

The subscripts "0" in Eq. (5) and (6) represent the absence of TEMPO. From these dynamic equations, the following Stern-Volmer equation can be obtained (Eq. (9)).

$$\begin{aligned}\frac{I_{DQH_0^{\cdot}}}{I_{DQH^{\cdot}}} &= 1 + \frac{k_q}{^3T_1^{-1} + k_r}[TEMPO] = 1 + k_q\tau[TEMPO] \\ &= 1 + k_s[TEMPO]\end{aligned} \tag{9}$$

Where

$$\tau = \frac{1}{^3T_1^{-1} + k_r} \tag{10}$$

$$k_s = k_q\tau \tag{11}$$

In Eq. (9), $I_{DQH_0^{\cdot}}$ and $I_{DQH^{\cdot}}$ represent the CIDEP intensity of $DQH^{\cdot}$ in the absence and presence of TEMPO, respectively. τ is the lifetime of $^3DQ^*$ in EG actually (see below). From Eq. (9), we can see that the ratio $I_{DQH_0^{\cdot}}/I_{DQH^{\cdot}}$ varies linearly with the variation of TEMPO concentration and the slope is k_s. From the definition (11), it can be seen that if we want to determine the quenching rate constant k_q, the slope k_s of Stern-Volmer plot and the lifetime τ of $^3DQ^*$ in EG must be measured in advance.

3.2. Quenching Rate Constant of $^3DQ^*$ by TEMPO in EG

In order to get the $I_{DQH_0^{\cdot}}/I_{DQH^{\cdot}} \sim [TEMPO]$ Stern-Volmer plot and the corresponding slope k_s, we measured the CIDEP spectra of photolysis of DQ in EG with different TEMPO concentrations we measured. The ratio value $I_{DQH_0^{\cdot}}/I_{DQH^{\cdot}}$ under each TEMPO concentration has also been calculated, which are listed in Table 1. From Table 1, it can be seen that the ratio value $I_{DQH_0^{\cdot}}/I_{DQH^{\cdot}}$ increases with the increase in the concentration of TEMPO. This is easy to understand, because the increase of TEMPO concentration increases its quenching to $^3DQ^*$ and decreases the hydrogen transfer reaction between

TABLE 1 **Dynamic Parameters of Photolysis of DQ/TEMPO in EG**

[TEMPO]/ mmol L^{-1}	$I_{DQH_0^{\cdot}}/I_{DQH}$	$k_s/10 \cdot L \cdot mol^{-1}$	$\tau/\mu s$	$k_q/Lmol^{-1}s^{-1}$
2	1.10	7.80	2.98	2.62×10^7
4	1.21			
6	1.41			
8	1.59			
10	1.77			

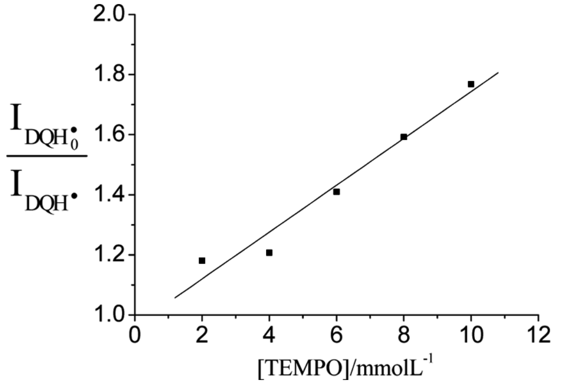


FIGURE 3 **Stern-Volmer plot of $I_{DQH_0}/I_{DQH^\cdot}$ versus [TEMPO] in EG.**

^{3}DQ* and EG. Fig. 3 is the Stern-Volmer plot of $I_{DQH_0^\cdot}/I_{DQH^\cdot}$ as a function of TEMPO concentration. The fttted slope k_s of this Stern-Volmer plot is also listed in Table 1.

In order to get the quenching rate constant k_q, we need further to obtain the lifetimeτ of ^{3}DQ* in EG with the absence of TEMPO. Fig. 4 is the transient absorptive spectrum of laser photolysis of DQ/EG solution. The broad transient absorptive peak at 460 nm can be attributed to ^{3}DQ*.[8] It can be seen that concurrent with decay of the ^{3}DQ* absorption is the formation of a peak at 420 nm, which can be assigned to DQH.[8] It is obvious that the reaction here is a hydrogen atom transfer reaction from EG to ^{3}DQ*, which indicates further that the reaction mechanism Eqs. (1)~(3) according to CIDEP spectrum is reasonable. From Eqs. (2) and (3), the decay equation of ^{3}DQ* after laser excitation can be written as Eq. (12).

$$\frac{d[^3DQ^*]}{dt} = -(k_d + {}^3T_1^{-1})[^3DQ^*] \qquad (12)$$

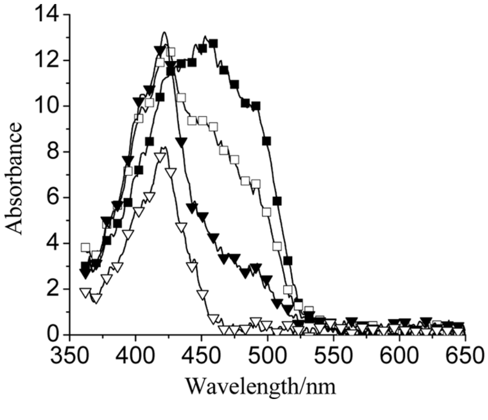


FIGURE 4 **Transient absorptive spectrum after 355 nm laser excitation of DQ in EG measured at 0.3 μs (■), 1.5 μs (□), 3.8 μs (▲), and 100 μs (△) after laser excitation.**

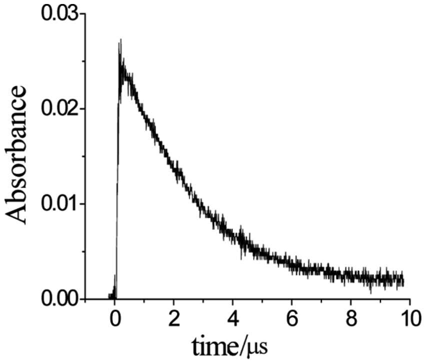


FIGURE 5 **Decay of the transient absorbance of ^{3}DQ* at 460 nm.**

Then the decay expression of ^{3}DQ* with time is

$$\begin{aligned}[^3DQ^*] &= [^3DQ^*]_0 \exp[-(k_d + {}^3T_1^{-1})t] \\ &= [^3DQ^*]_0 \exp[-t/\tau] \qquad (13)\end{aligned}$$

Here $[^3DQ^*]_0$ is the initial concentration of ^{3}DQ* before decay and τ is $1/(^3T_1^{-1} + k_r)$. From expression (13), it can be seen that if $t = \tau$, $[^3DQ^*]$ decrease to $[^3DQ^*]_0/e$. So the lifetime is τ. Figure 5 is the decay of the transient absorbance of ^{3}DQ* at 460 nm and the fitted lifetime τ can be seen in Table 1. Since the slope k_s and lifetime τ of ^{3}DQ* have been determined, the quenching rate constant k_q of ^{3}DQ* by TEMPO in EG can be obtained simply from formula (11), which is shown in Table 1.

3.3. Viscosity Effect on the Quenching of ^{3}DQ* by TEMPO

To investigate the influence of solvent viscosity to the quenching dynamics of ^{3}DQ* by TEMPO, the photolysis experiments of DQ/TEMPO were performed in various solvents with different viscosities. These solvents are PG and the mixtures of EG and PG with different ratios in volume and their viscosity are shown in Table 2.[16] Using the same method

TABLE 2 **Quenching Rate Constants of ^{3}DQ* by TEMPO in Different Solvent**

Solvent	Viscosity (10^{-2} Pa s)	K_q (L mol^{-1} s^{-1})
EG	1.16	2.62×10^7
80% EG-20% PG	1.71	2.30×10^7
40% EG-60% PG	2.02	1.85×10^7
20% EG-80% PG	2.58	1.46×10^7
PG	3.03	1.20×10^7

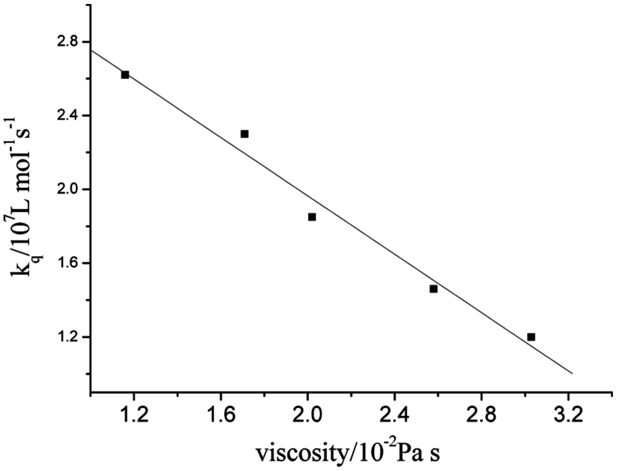


FIGURE 6 Plot of the quenching rate constant of $^3DQ^*$ by TEMPO k_q versus solvent viscosity.

used in solvent EG, the CIDEP spectra of photolysis of DQ without TEMPO and with different TEMPO concentration in each solvent were measured, respectively. The transient absorptive spectra of DQ in each solvent was also recorded. According to these CIDEP spectra and the decay curves of transient absorbance of $^3DQ^*$, the slope k_s of Stern-Volmer plot, the lifetime τ of $^3DQ^*$, and the corresponding quenching rate constant of $^3DQ^*$ by TEMPO in each solvent are obtained, which are listed in Table 2. The method used here is the same as in EG.

From Table 2, it can be seen that the quenching rates of $^3DQ^*$ by TEMPO are in the order of $10^7 \, Lmol^{-1} s^{-1}$. However, the second order rate constants for reaction of $^3DQ^*$ with $PASCH_2$ in ethanol and in acetonitrile were reported to be diffusion-controlled $1.75 \times 10^9 \, Lmol^{-1} s^{-1}$ and $3.46 \times 10^9 \, Lmol^{-1} s^{-1}$, respectively.[7] Compared to these reaction rate constants, the quenching rate constant of $^3DQ^*$ by TEMPO in this work is 10^2 times less. It is well known that the reaction rate of diffusion controlled reaction is mainly determined by the diffusion rate of reactants in solution, while the diffusion coefficient satisfies the Stokes-Einstein relation

$$D = \frac{k_B T}{6\pi\eta r} \tag{14}$$

where, k_B is the Boltzmann constant, η is the solvent viscosity, and r is the radius of the diffusive particle. In fact, the viscosity of ethanol and acetonitrile are 9.97×10^{-4} Pa s[16] and 3.4×10^{-4} Pa s[31] at room temperature, but the viscosity here are at least 20 times larger. Thus, it is possible that the quenching rate constant of $^3DQ^*$ by TEMPO in PG is in the order of $10^7 \, Lmol^{-1} s^{-1}$. Therefore, the quenching of $^3DQ^*$ by TEMPO here are still close to be diffusion-controlled.

In addition, it can be seen that the quenching rate of $^3DQ^*$ by TEMPO decreases with the increase in solvent viscosity (Fig. 6). It is easy to understand this because the diffusion coefficient is inversely proportional to solvent viscosity. Although it is not accurately relation between the quenching linear rate constant and solvent viscosity, it is a linear relation in our experimental viscosity range.

4. CONCLUSION

In summary, the CIDEP spectrum and transient absorptive spectrum have been recorded to measure the quenching rate constant of $^3DQ^*$ by TEMPO in a different solvent. The quenching rate constants were obtained through the Stern-Volmer plot of the quenching of $^3DQ^*$ by TEMPO and the transient absorbance decay of ^3DQ. When the solvent viscosity increases from 1.16×10^{-2} Pa s to 3.03×10^{-2} Pa s, the quenching rate constant decreases from $2.89 \times 10^7 \, L mol^{-1} s^{-1}$ to $1.20 \times 10^7 \, L mol^{-1} s^{-1}$. These quenching rate constants are diffusion-controlled and viscosity-dependent. The quenching rate constant decreases linearly with the increase in solvent viscosity in the range used in our experiment.

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