Chemically induced dynamic electron polarization investigation of the triplet-radical system in the solution of the triplet quencher

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The chemically induced dynamic electron polarization (CIDEP) of the triplet molecule/triplet quencher/2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) systems were measured using the high time-resolved ESR spectrometer. The competition between the radical-triplet pair mechanism (RTPM) and triplet mechanism (TM) or radical pair mechanism (RPM) polarization in the solution of the triplet quencher was investigated, and the relationship between reaction rate of the radical-triplet pair and quenching rate of triplet was deduced.

Keywords   Chemically induced dynamic electron polarization, triplet-radical pair mechanism, triplet quenching

Introduction

Using high power laser, the polarized triplet states with high concentration can be generated through inter-system crossing between excited singlet states and triplet states of the molecule. In addition, if the stable radicals exist in the solution, the triplet-doublet pairs ($^3 T\text{-}^2 R$) can be formed when the radicals encounter with triplet molecules. The pairs ($^3 T\text{-}^2 R$) are either in the quartet spin states or doublet spin states. Through mixing between the quartet and doublet spin states of the pairs, the chemically induced dynamic electron polarization (CIDEP) of the stable radical can be generated, and it is referred as the radical-triplet pair mechanism (RTPM).[1] 2,2,6,6-Tetramethyl-1-piperidinyloxyl (TEMPO) is frequently used as the stable radical. When laser irradiates the photosensitive molecule/TEM-

PO system in the alcohol's solution, the CIDEP signal of TEMPO can be obtained. On the other hand, if photo-excited triplet states can be quenched by solvent molecule where there exists a hydrogen donor group, the polarized triplet molecule radical and the polarized solvent molecule radical are generated through hydrogen atom abstraction from solvent by excited triplet molecule. This is a polarization process, which leads to triplet quenching and polarized radical pair.[2] In the photosensitive/TEMPO solution with triplet state quencher, there are therefore both RTPM and triplet quenching polarization. Obviously, the competition between RTPM polarization and triplet quenching polarization will occur.

Using high time-resolved ESR spectrometer, the CIDEP of the triplet molecule/triplet quencher/TEMPO systems were measured, and the competition between RTPM and triplet quenching polarization process were investigated.

Experimental

The CIDEP experiments were performed using a homemade X-band time-resolved ESR spectrometer without field modulation.[3] It mainly consists of a balanced mixer with the zero beat frequency as the microwave signal receiver, a reflection klystron as the microwave source at about 9400 MHz, and a rectangle sample cavi-
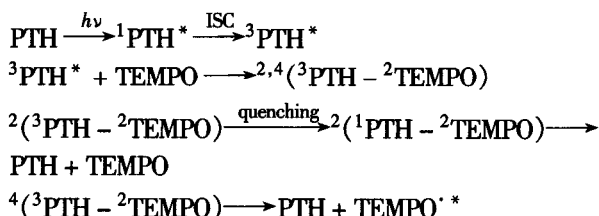
ty of TE$_{102}$ with Q factor about 2000. The CIDEP signal from the balanced mixer was amplified by a wideband differential amplifier with 50 ns response, and then input to a digital oscilloscope to record TR-ESR signal, or input to a boxcar to record CIDEP spectrum. The boxcar gate was 0.3 μs. The flash source was provided by an excimer laser operated at 308 nm (XeCl). The width and the energy of the laser pulse were 18 ns and 60 mJ, respectively.

p-Benzoquinone (PBQ), anthraquinone (AQ), phenothiazine (PTH) and benzaldehyde (BA) were used as photosensitive molecules, TEMPO as stable radical and ethylene glycol (EG) or the mixer of ethylene glycol and H$_2$O as solvent. The PBQ and AQ were purified by vacuum sublimation, BA and PTH were used as received without further purification. The sample solution was flowed through a flat quartz cell (0.3 mm light path) after deoxygenating by bubbling the pure N$_2$.

Results

PTH/TEMPO/EG *system*

There was no CIDEP signal after laser flash of PTH in ethylene glycol (EG), but a TR-ESR signal was obtained after laser excitation in the PTH/TEMPO/EG system as shown in Fig. 1. The hyperfine structure of total emissive CIDEP signal with triplet splitting was obtained. The observed TR-ESR spectrum can be attributed to TEMPO radical,[4] and interpreted by following reaction:

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

$${}^3PTH^* + TEMPO \longrightarrow {}^{2,4}({}^3PTH - {}^2TEMPO)$$

$${}^2({}^3PTH - {}^2TEMPO) \xrightarrow{quenching} {}^2({}^1PTH - {}^2TEMPO) \longrightarrow PTH + TEMPO$$

$${}^4({}^3PTH - {}^2TEMPO) \longrightarrow PTH + TEMPO^{\cdot *}$$

where ${}^1PTH^*$ and ${}^3PTH^*$ represent excited singlet and triplet states of PTH, respectively, ISC stands for "intersystem crossing", according to RTPM theory ${}^3PTH^*$ and TEMPO can form encounter complexes ${}^3PTH^*$-TEMPO, which shows the quartet or doublet spin states. The doublet state results in a singlet molecule and a doublet radical, which is an unpolarized process. While the quartet states results in polarization

of TEMPO due to the interaction of radical and triplet molecule. This paper reports the results of this experimental research.
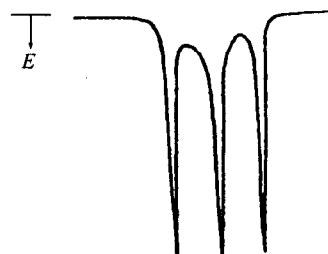

Fig. 1   TR-ESR signal of the PTH/TEMPO/EG system after laser excitation.

AQ(PBQ, BA)/TEMPO/EG *system*

The TR-ESR signal obtained by the 308 nm-laser flash of AQ in ethylene glycol (EG) is shown in Fig. 2a. The observed signal consists of the CIDEP spectrum of anthrasemiquinone radical AQH$^{\cdot}$ and the ethylene glycol ketyl radical R$^{\cdot}$ due to hydrogen atom abstraction from EG by excited triplet anthraquinone.[5] The CIDEP signal of R$^{\cdot}$ shows the hyperfine structure with six double-lines. Its two more intense emission lines lie in the low field, two weaker absorption lines lie in high field, and the other two lines in the middle field is overlapped on a wide peak, which was attributed to AQH$^{\cdot}$ radicals. When TEMPO was added into AQ/EG solution, besides the polarized spectra of AQH$^{\cdot}$ and R$^{\cdot}$, three hyperfine emission lines can be obtained after laser excitation, which is the same as that in PTH/TEMPO/EG system as shown in Fig. 2b. The ${}^3\overline{AQ^* - TEMPO}$ complexes in AQ/TEMPO/EG were formed when ${}^3AQ^*$ encountered TEMPO, and therefore the RTPM polarization of TEMPO was generated.

The experimental results show that the intensity of the polarized signals of AQH$^{\cdot}$, R$^{\cdot}$ and TEMPO radicals changes with the concentration of TEMPO in the solution. When the concentration of TEMPO radical increases, the intensity of the polarized signals of AQH$^{\cdot}$ and R$^{\cdot}$ radicals gradually decreases to zero, while the intensity of TEMPO radical increases to the maximum.

Using the same method, the CIDEP spectra of the PBQ/TEMPO/EG and BA/TEMPO/EG systems were measured. The TR-ESR spectra of PBQ/EG and PBQ/TEMPO/EG systems are shown in Fig. 3a and Fig. 3b, respectively. The polarized spectra of PBQH$^{\cdot}$ and R$^{\cdot}$

radicals in the PBQ/EG system can be interpreted by the triplet polarization mechanism. The TR-ESR spectra in BA/EG and BA/TEMPO/EG are shown in Fig. 4a and Fig. 4b, respectively. From Fig. 4a one can seen that the CIDEP spectrum of R˙ radicals was E/A (emission

in the low field and absorption in the high field) polarization, which was the radical pair polarization mechanism, but the polarized signal of the BA radical was not measured due to its fast relaxation.
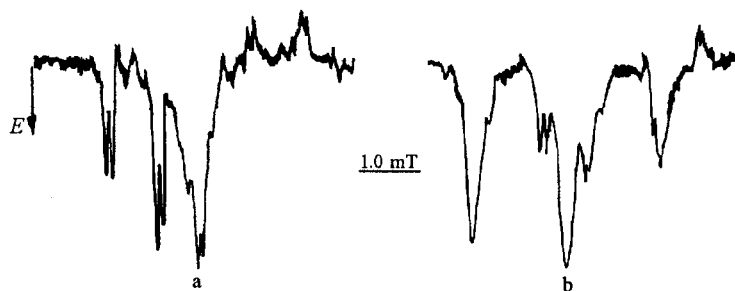

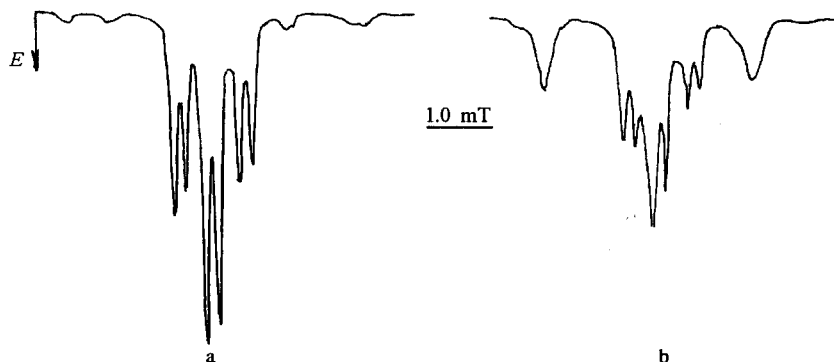**Fig. 2**　TR-ESR spectra of AQ/EG (a) and AQ/TEMPO/EG (b), [TEMPO]: 2 mmol·L^{-1}.

Fig. 3　TR-ESR spectra of PBQ/EG (a) and PBQ/TEMPO/EG (b), [TEMPO]: 2 mmol·L^{-1}.

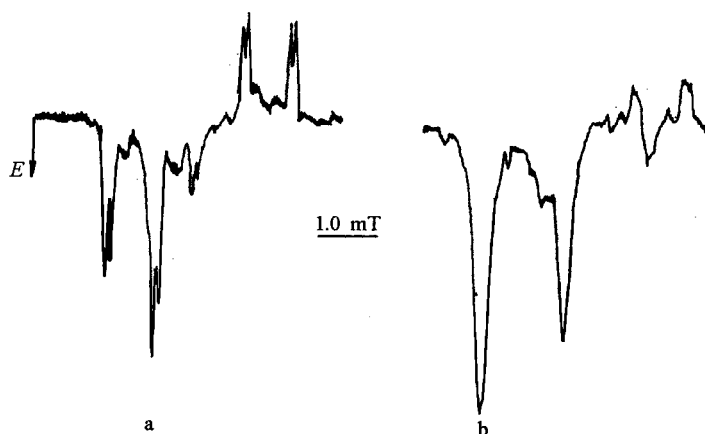**Fig. 4**　TR-ESR spectra of BA/EG (a) and BA/TEMPO/EG (b),[TEMPO]: 20 mmol·L^{-1}.

For these two systems, the dependence of the intensity of the polarized signals of AQH˙ and PBQH˙ radicals on the concentration of TEMPO radical in the solution was the same as that of AQH˙ and R˙ radicals in the AQ/TEMPO/EG system.

I_{Q0} is defined as the intensity of polarization signal

of the quenching reaction radical MH˙, which is AQH˙, PBQH˙ or R˙ radicals for the different system in the absence of TEMPO, and I_Q as the intensity of polarization signal of the quenching reaction radical in the presence of TEMPO. According to the previous experimental results, I_Q decreases with the increase of the TEMPO con-

centration, and then the ratio of I_{QO}/I_Q will increase. I_{QO}/I_Q *vs*. the concentration of TEMPO was plotted in Fig. 5.

From Fig. 5, the linear relationship of I_{QO}/I_Q with the concentration of TEMPO is shown. The following e-quation is true:

$$\frac{I_{QO}}{I_Q} = 1 + k_D[\text{TEMPO}] \qquad (1)$$

The constant k_D is the slope of the line and reflect-ed the relation between the reaction rate of the radical-triplet pair and the quenching rate of the triplet. The smaller k_D shows the slower intensity decreases of quenching reaction radical.
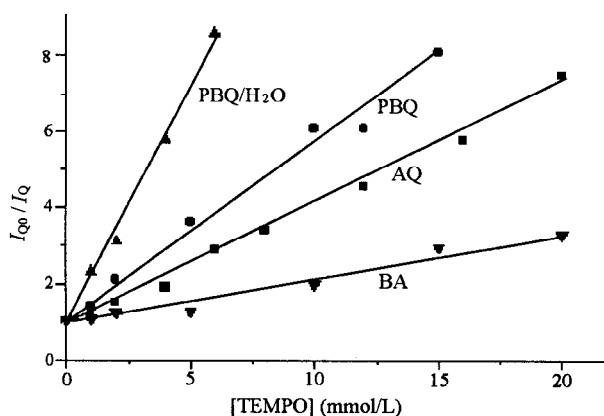

Fig. 5 I_{QO}/I_Q *vs*. [TEMPO] in different system (Y axis is the ratio of the intensity of the quenching reaction radical with and without TEMPO, respectively, X axis [TEM-PO] the concentration of TEMPO).

Discussion

In triplet quencher solution, if k_q represents the quenching rate of the triplet by the solvent molecule, $^3T_1$ represents the spin-lattice relaxation time of triplet states, the reaction rate equation can be obtained as fol-lows:

$$\frac{d[\text{MH}^\cdot]}{dt} = k_q[^3\text{M}^\cdot] \qquad (2)$$

$$-\frac{d[^3\text{M}^*]}{dt} = {}^3T_1^{-1}[^3\text{M}^*] + k_q[^3\text{M}^*] \qquad (3)$$

As TEMPO radical presents in solution, the com-petition between the k_q and $^3T_1$ and the reaction rate k_r of triplet-TEMPO may occur, and the rate equation is obtained as follows:

$$\frac{d[\text{MH}^\cdot]}{dt} = k_q[^3\text{M}^*] \qquad (4)$$

$$-\frac{d[^3\text{M}^*]}{dt} = {}^3T_1^{-1}[^3\text{M}^*] + k_q[^3\text{M}^*] + \\ + k_r[^3\text{M}^*][\text{TEMPO}] \qquad (5)$$

From Eqs. (4) and (5), the concentration of rad-ical MH$^\cdot$ can be expressed as:

$$[\text{MH}^\cdot] = \frac{k_q[^3\text{M}^*]_0}{{}^3T_1^{-1} + k_q + k_r[\text{TEMPO}]}\{1 - \exp[^3T_1^{-1} + \\ + k_q + k_r[\text{TEMPO}])t]\} \qquad (6)$$

where [MH$^\cdot$] represents the concentration of the quenching reaction radical MH$^\cdot$ in the presence of TEM-PO. From Eqs. (2) and (3), the concentration [MH$^\cdot$]$_0$ of radical MH$^\cdot$ in the absence of TEMPO can be expressed as:

$$[\text{MH}^\cdot]_0 = \frac{k_q[^3\text{M}^*]_0}{{}^3T_1^{-1} + k_q}\{1 - \exp[-({}^3T_1^{-1} + k_q)t]\} \qquad (7)$$

The exponential term in the Eqs. (6) and (7) is small-er than 10^{-3}, and therefore can be neglected, so:

$$\frac{[\text{MH}^\cdot]_0}{[\text{MH}^\cdot]} = 1 + \frac{k_r}{{}^3T_1^{-1} + k_q}[\text{TEMPO}] \qquad (8)$$

P_{QO} and P_Q are defined as the polarized intensity of the quenching reaction radical in the absence and the pres-ence of TEMPO, respectively, and P_{QO}/P_Q is linear against the concentration of TEMPO,

$$\frac{P_{QO}}{P_Q} = \frac{[\text{MH}^\cdot]_0}{[\text{MH}^\cdot]} = 1 + \frac{k_r}{{}^3T_1^{-1} + k_q}[\text{TEMPO}] \qquad (9)$$

Comparing Eqs. (1) and (9), one obtain:

$$k_D = \frac{k_r}{{}^3T_1^{-1} + k_q} \qquad (10)$$

Using previous data, the reaction rate k_r of the radical-triplet pair can be deduced, and some results are listed in Table 1.

From the Table, one can find that the reaction rate k_r of $^3\text{AQ}^*$ and TEMPO in AQ/EG/TEMPO is smaller

than that of ^{3}PBQ* and TEMPO in PBQ/EG/TEMPO. This indicates that the decrease rate of intensity of quenching reaction radical AQH* in AQ/EG/TEMPO is

smaller than that of PBQH$^.$ in PBQ/EG/TEMPO. It is consistent with the experiment.

Table 1   Constants k_D and reaction rates k_r of the radical-triplet pair

Samples	k_D $[1 \cdot (\text{mol/L})^{-1}]$	$^3T_1^{-1}$ (s^{-1})	k_q (s^{-1})	k_r $[1 \cdot (\text{mol/L})^{-1} \cdot \text{s}^{-1}]$
AQ/TEMPO/EG	3.2×10^2	3.3×10^6 [6,7]	3.39×10^6 [6,7]	2.14×10^9
PBQ/TEMPO/EG	4.6×10^2	5.1×10^6 [6,8]	7.9×10^6 [6,8]	6.0×10^9
PBQ/TEMPO/H$_2$O/EG	6.79×10^2	5.1×10^6 [6,8]	—	—
BA/TEMPO/EG	1.18×10^2	—	—	—

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