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Time-resolved ESR study of electron transfer process between phenothiazine and maleic anhydride

Guanglong He [a], Xinyue Li [b], Junlin Yang [c], Ciping Chen [d], Guangzhi Xu [a,*]

[a] *Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China*
[b] *Department of Chemistry and Chemical Engineering, Dalian University, Dalian 116012, People's Republic of China*
[c] *Institute of Biophysics, Chinese Academy of Sciences, Beijing 100101, People's Republic of China*
[d] *Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing 100101, People's Republic of China*

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Abstract

The electron transfer reaction between phenothiazine (PTH) and maleic anhydride (MA) as well as the related chemically induced dynamic electron polarization (CIDEP) effect has been investigated by time-resolved electron spin resonance (TRESR). The CIDEP spectra assigned to the anion radical ($MA^{\bullet -}$) of maleic anhydride reveal that the reaction takes place in the excited triplet state of PTH. The electron transfer rate constant k_{ET} and the spin-lattice relaxation time $^3\tau_1$ of the excited triplet state of PTH are 3×10^8 M^{-1} s^{-1} and 10^{-7} s, as obtained from our TRESR experiment. © 1997 Elsevier Science S.A.

Keywords: TRESR; Electron transfer; CIDEP

1. Introduction

It is well known that the phenothiazine drugs now play a very important role in chemotherapy. Their biological activities may be due to charge transfer processes. The photochemical oxidation of phenothiazine and its derivatives, especially the light-induced formation of stable and transient radicals of phenothiazine and its derivatives attract attention continuously [1–3]. The conventional method for detection and identification of such transient radicals is the spin-trapping technique that involves trapping of a reactive free radical via an addition reaction to produce a more stable radical detectable by electron spin resonance (ESR) whose hyperfine splitting parameters permit the identification of the initial radical trapped [4–12]. Unfortunately, the usual spin-trapping technique is not time-resolved, so it cannot give transient information about the dynamic process of light-induced electron transfer reactions. However, the time-resolved electron spin resonance (TRESR) technique has been shown to be an effective and direct method to detect and identify transient radicals with short lifetime and low concentration [13,14].

In the present paper, the TRESR method has been employed to study the mechanism of photo-induced electron transfer between the electron donor phenothiazine (PTH) and the electron acceptor maleic anhydride (MA) as well as the related chemically induced dynamic electron polarization (CIDEP) effect.

2. Experimental

2.1. Chemical reagents

Ethylene glycol (RH) was distilled several times. Anthracene (AN) was sublimated several times. Acridine, phenothiazine (PTH) and maleic anhydride (MA) were recrystallized from ethanol and benzene several times respectively.

2.2. The detection of CIDEP signals

The X-band TRESR spectrometer with a time resolution of 200 ns was described elsewhere [15]. The experimental arrangement comprised a Nd:YAG laser (355 nm, 20 ns pulse width, ≈ 10 mJ pulse energy), a boxcar integrator (EG and G 4400-1) and a digital oscilloscope (HP5460). The transient ESR signals obtained without field modulation were transferred to the boxcar integrator for spectrum measurements and to the digital oscilloscope for CIDEP time profiles. After deoxygenation with bubbling pure nitrogen gas, the

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[*] Corresponding author.

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sample solutions were exposed to laser irradiation while flowing through a flat quartz cell (0.3 mm optical path length) within the ESR cavity with a flow rate of 9 ml min^{-1}. All TRESR measurements were carried out at room temperature.

2.3. Triplet quantum yield measurements

The pulsed laser photoacoustic calorimeter has been described previously [16,17]. It comprised the above mentioned Nd:YAG laser, a home-made photoacoustic transducer, an amplifier, and a digital oscilloscope (HP5460) connected to a microcomputer (486-50) through a RS232 interface. The laser energy was kept below 100 μJ per pulse to avoid any nonlinear effects in the illuminated sample solutions. Absorbance A of samples or reference compounds was determined by using a Hitachi-340 spectrometer. The fluorescence spectrum and fluorescence quantum yield Φ_f were determined by using a Hitachi-MPF-4 fluorescence spectrometer. Rhodamine 6G ($\Phi_f = 0.95$) was used as reference to determine Φ_f of phenothiazine [18].

3. Results and discussions

3.1. TRESR

Before and after irradiation with the 355 nm laser beam, the solution of phenothiazine or maleic anhydride in ethylene glycol showed no CIDEP signals. Before irradiation, the solution of phenothiazine and maleic anhydride in ethylene glycol showed no CIDEP signals either. But after irradiation, the phenothiazine–maleic anhydride system gave a TRESR spectrum obtained by time integration between 2 and 2.299 μs at [MA] = 200, 100, 50, 20 mM, as shown in Fig. 1. This spectrum consisted of an emissive (E) triplet with a hyperfine splitting constant of 0.57 mT and intensity ratio of nearly 1:2:1. The spectrum might arise from a transient radical having two equivalent protons.

Firstly, from the measured UV–vis absorption spectra it is known that maleic anhydride has no absorption at 355 nm, while phenothiazine can be excited at 355 nm to its first singlet state ^{1}PTH. Then, ^{1}PTH intersystem crosses to first excited triplet state ^{3}PTH with a triplet quantum yield of $\Phi_T = 0.86$. The details of the quantum yield measurement will be stated in the next section. With the aid of the following simplified Rehm–Weller relation [19]:

$$\Delta G = 23.06[E(\mathrm{D/Dv}^{\cdot+}) - E(\mathrm{A/A}^{\cdot-})] - E(\mathrm{D}^*)\ \mathrm{kcal\ mol}^{-1} \qquad (1)$$

the Gibbs free energy change ΔG of the electron transfer reaction of ^{1}PTH or ^{3}PTH with MA can be calculated. In the above equation, $E(\mathrm{D/D}^{\cdot+})$ (V) and $E(\mathrm{A/A}^{\cdot-})$ (V) are the oxidation and reduction potentials of the electron donor and acceptor respectively. $E(\mathrm{D}^*)$ (kcal mol^{-1}) is the energy of the electronically excited state of the electron donor. Given $E(\mathrm{PTH/PTH}^{\cdot+}) = 0.23$ V (vs. SCE) [20], $E(\mathrm{MA/MA}^{\cdot-}) = -0.88$ V (vs. SCE) [20,21], $E(^1\mathrm{PTH}) = 83.02$ kcal mol^{-1} and $E(^3\mathrm{PTH}) = 62.03$ kcal mol^{-1} [22], the calculated ΔG of the electron transfer reactions of ^{1}PTH and ^{3}PTH with MA are −57.42 and −36.43 kcal mol^{-1} respectively. Therefore, it would be thermodynamically allowed to produce radical MA$^{\cdot-}$ and PTH$^{\cdot+}$ from the electron transfer reaction between ^{1}PTH or ^{3}PTH and MA. According to the number and the hyperfine splitting constant of the hyperfine lines as shown in Fig. 1, the observed spectrum stems from MA$^{\cdot-}$.

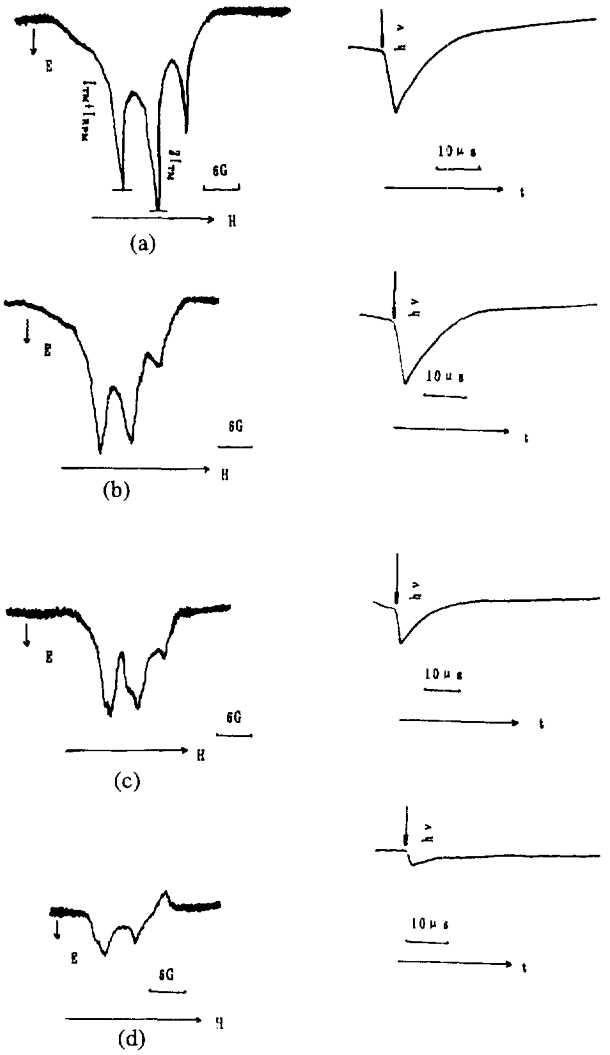

Fig. 1. The CIDEP spectra and the time profiles of the $M_I = 0$ lines of 20 mM PTH with (a) 200 mM (b) 100 mM (c) 50 mM (d) 20 mM of MA in ethylene glycol after 355 nm laser irradiation. The door width of the boxcar was 299 ns; the delay time of the door opening after the laser flash was 2 μs.

Secondly, we will rationalize why the TRESR spectrum of radical MA$^{\cdot-}$ shows emissive CIDEP signals as follows. Absorption of a photon by the ground state PTH molecule yields an excited singlet state ^{1}PTH which may intersystem cross to a triplet excited state ^{3}PTH* whose Zeeman levels T_{+1}, T_0 and T_{-1} are non-degenerate in the magnetic field of the ESR spectrometer. It is well known that the intersystem crossing process is selective and creates spin polarization in triplet state molecule. If the electron transfer from ^{3}PTH* to MA (with a rate constant k_{ET}) is fast enough to compete with the triplet spin–lattice relaxation process with rate constant $k_{T1} = 1/{}^3\tau_1$ (where $^3\tau_1$ is the triplet spin–lattice relaxation time of ^{3}PTH*), then the spin polarization of ^{3}PTH* will be carried over by spin conservation to the radical $MA^{\bullet -}$, where the spin polarization is frozen by its much slower spin–lattice relaxation rate. This kind of spin polarization transfer only takes place when the electron transfer reaction is sufficiently fast. This is the so-called triplet mechanism (TM) of CIDEP as shown in the literature [13,14].

By careful inspection of the spectrum of radical $MA^{\bullet -}*$ in Fig. 1, we find that the intensity ratio of the hyperfine lines deviate from 1:2:1, the low field line of the triplet is more intense than the high field one. That is to say, the strong emissive pattern (E) of spin polarization component I_{TM} by the triplet mechanism (TM) is superimposed a weak emissive/absorptive (E/A) pattern of spin polarization component I_{RPM} by the S–T mixing of radical pair mechanism (RPM) [13,14], which is usually observable in many photochemical systems [23]. The definitions of I_{TM} and I_{RPM} are given in Fig. 1(a), where the intensity ratio of the TM polarization of each hyperfine line is $-1:-2:-1$ (negative sign means emission) from the low field to high field side and that of the RPM polarization of each hyperfine line is $-1:0:+1$ (positive sign means absorption). In addition, this kind of deviation and in turn, the ratio I_{TM}/I_{RPM} depends on the concentration [MA]. Based on the above analysis, the relationship of ratio I_{TM}/I_{RPM} and [MA] may be expressed approximately by the equation [23]:

$$I_{TM}/I_{RPM} = C\exp[-k_{T1}/(k_{ET}[\mathrm{MA}])] \quad (2)$$

or

$$-\ln(I_{TM}/I_{RPM}) = -\ln C + k_{T1}/(k_{ET}[\mathrm{MA}]) \quad (3)$$

where C is a constant.

The linear dependence of $-\ln(I_{TM}/I_{RPM})$ on $[\mathrm{MA}]^{-1}$ shown in Fig. 2 supports the above prediction. The calculated k_{ET}/k_{T1} as derived from the slope of the plots in Fig. 2 is $k_{ET}/k_{T1} = 29.41\ \mathrm{M}^{-1}$. Because the electron transfer reaction between ^{3}PTH* and MA is diffusion controlled, k_{ET} is equal to the diffusion rate constant k_D. The relationship between k_D and temperature T and viscosity η is [24]:

$$k_D = 2\times10^5 T/\eta\ (\mathrm{M}^{-1}\ \mathrm{s}^{-1}) \quad (4)$$

where T is in kelvins and η is in Poise. Substituting the viscosity $\eta = 0.2$ Poise of ethylene glycol [25] and the experimental temperature $T = 298$ K into Eq. (4), the electron transfer rate constant k_{ET} ($\cong k_D$) and the triplet state spin–lattice relaxation time $^3\tau_1$ are calculated as $3\times10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and 10^{-7} s respectively.

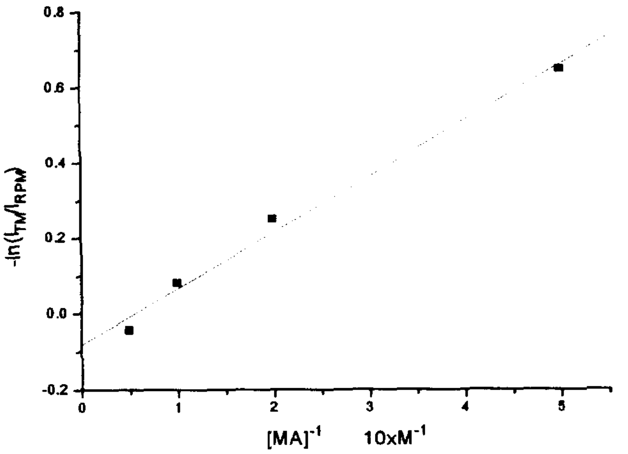

Fig. 2. The plots of the negative logarithm of I_{TM}/I_{RPM} against $[\mathrm{MA}]^{-1}$.

From the above discussion, it is obvious that electron transfer as well as spin polarization transfer between ^{3}PTH* and MA occurs simultaneously. The measured CIDEP signals originate from both TM and RPM, but the contribution of the former is larger than that of the latter. The overall photoinduced reaction mechanism may be expressed as follows:

$$\mathrm{PTH} \xrightarrow{h\nu_{ex}} {}^1\mathrm{PTH}$$

$$^1\mathrm{PTH} \xrightarrow{k_{ISC}} {}^3\mathrm{PTH}^* \xrightarrow{k_{T1}} {}^1\mathrm{PTH}$$

$$^3\mathrm{PTH}^* + \mathrm{MA} \xrightarrow{k_{ET}} \overline{^3\mathrm{PTH}^{\bullet +}\ \mathrm{MA}^{\bullet -}}\,*$$

$$\overline{3\mathrm{PTH}^{\bullet +}\ \mathrm{MA}^{\bullet -}}\,* \quad \overset{\text{S–T mixing}}{\rightleftarrows} \quad \overline{^1\mathrm{PTH}^{\bullet +} + \mathrm{MA}^{\bullet -}}\,*$$

$$\overline{1{,}3\mathrm{PTH}^{\bullet} + \mathrm{MA}^{\bullet -}}\,* \rightarrow \mathrm{PTH}^{\bullet +}* + \mathrm{MA}^{\bullet -}*$$

$$\mathrm{PTH}^{\bullet +}* + \mathrm{MA}^{\bullet -}* \rightarrow \text{Products}$$

In our experiment, a CIDEP signal of radical $\mathrm{PTH}^{\bullet +}*$ was not observed. This possibly is due to its too many hyperfine lines and the too fast a spin–lattice relaxation rate. But it is interesting to note that after the TRESR measurements mentioned above, the stable ESR signal of radical $\mathrm{PTH}^{\bullet +}$ could be observed easily. In contrast, the stable ESR signal of $\mathrm{MA}^{\bullet -}$ was not obtained. This is consistent with the fact that $\mathrm{MA}^{\bullet -}$ is unstable at room temperature [20,21].

3.2. *Quantum yield Φ_T of phenothiazine*

The experimentally measured photoacoustic signal V_{pa} is given by [16–18,26]:

$$V_{pa} = k\Phi_{nr}E_L(1-10^{-A}) \quad (5)$$

or

$$V_{pa} = k\Phi_{nr}E_L A \quad (6)$$

where k is a constant which depends on the geometry of the experimental set-up and the thermoplastic quantities of the medium. Here E_L is the incident laser pulse energy, Φ_{nr} is the fraction of the laser energy absorbed by PTH released nonradiatively as the thermal energy within the response time of the detector of the photoacoustic calorimeter. A is the absorbance (or optical density) of the sample solution. For low

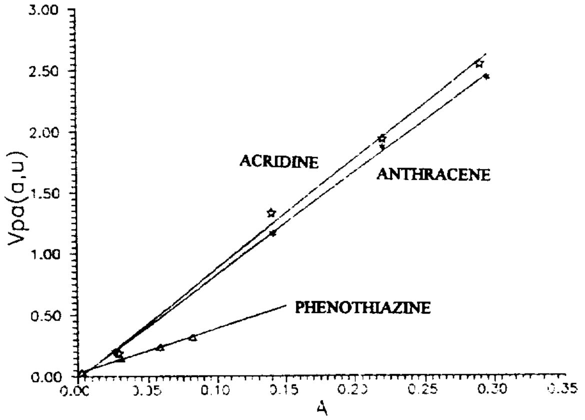

Fig. 3. Linear dependence of the V_{pa} (a.u.) signal on the absorbance A for the optical path length $L=10^{-2}$ cm for anthracene (∗), acridine (☆) and phenothiazine (△) solutions in ethylene glycol.

Table 1

Φ_{nr} and Φ_T of phenothiazine determined by photoacoustic calorimetric measurement

Compound	Φ_f	$h\nu_f$ (cm^{-1})	E_T (cm^{-1})	Φ_{nr}	Φ_T
Anthracene	0.27	24900	14900	0.44	0.66 ± 0.05
Acridine	0.03	23250	15850	0.47	0.82 ± 0.05
Phenothiazine	0.24	22483	21503	0.192	0.86 ± 0.06

absorbance, $1-10^{-A} \cong A$, in this case, the photoacoustic signal V_{pa} is proportional to A rather than to $1-10^{-A}$.

If V_{pa} of samples with various absorbance is measured at constant E_L, then the plots of V_{pa} vs. $(1-10^{-A})$ or vs. A will yield a straight line with slope $=k\Phi_{nr}E_L$. By measuring V_{pa} under identical conditions for sample (PTH) and reference (anthracene or acridine) with known Φ_{nr} and from the ratio of the slope of V_{pa} vs. A for sample and reference as shown in Fig. 3, the Φ_{nr}(PTH) obtained from Eq. (7) is listed in Table 1.

$$\Phi_{nr}(\mathrm{PTH}) = \mathrm{slope}(\mathrm{PTH}) \times \Phi_{nr}(\mathrm{reference}) / \mathrm{slope}(\mathrm{reference}) \quad (7)$$

Furthermore, we use the following well-known energy balance relation [26,27]:

$$\Phi_{nr} = 1 - \Phi_f h\nu_f / E_L - \Phi_T E_T / E_L \quad (8)$$

where the term $\Phi_f h\nu_f / E_L$ represents the fraction of absorbed energy emitted in form of fluorescence ($h\nu_f$ is the average fluorescence photon energy) and the term $\Phi_T E_T / E_L$ represents the fraction of absorbed energy stored in the triplet state. After substituting the values of Φ_{nr}, Φ_f and $h\nu_f$ determined for phenothiazine into Eq. (8), the quantum yield Φ_T of triplet state (^{3}PTH*) formation derived from photoacoustic calorimetric determination is obtained and is listed in Table 1.

The large value of Φ_T of PTH reveals that most of the excited singlet state ^{1}PTH molecules intersystem cross to the excited triplet state ^{3}PTH molecules, and provides further confirmation of the TM and RPM as indicated above.

Acknowledgements

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