

Time-resolved laser flash photolysis study on transient reaction between excited triplet state of anthraquinone derivatives (AQS) and 2-deoxythymidine

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ABSTRACT

The transient absorption spectra and kinetics of excited triplet state of anthraquinone derivatives 2-anthraquinonesulfonatesodium (AQS) and 2-deoxythymidine (dT) have been investigated in CH₃CN-H₂O (97:3) using the time-resolved laser flash photolysis technique (KrF, 248 nm). The absorption spectra of dT radical cation and the radical anion of AQS have been observed. From dynamic and thermodynamic analysis, the mechanism of this transient reaction has been initially analysed.

KEYWORDS

2-Anthraquinonesulfonatesodium (AQS);
2-Deoxythymidine; Transient Reaction; Laser
Flash Photolysis

1. INTRODUCTION

Quinones play central roles in aerobic respiration and energy-yielding photosynthesis [1]. The “strong sensitizer” 2-anthraquinonesulfonatesodium (AQS), has received much attention because of its relevance to some important photosensitizing effects induced by anthraquinones, phototendering of cellulosic materials. Recently, interest in photobiology area has been heightened by suggestions for utilizing anthraquinones as photonuclease [2]. AQS is a strong sensitizer and for numerous investigations concerning on it [3-5], only a few studies have been performed on the reaction of AQS with biological substances [5]. Here we report that time-resolved spectro-

scopic and kinetic evidences for the interaction of AQS with dT in CH₃CN-H₂O solvent mixture were investigated using KrF laser flash photolysis. The transient absorption spectra and kinetics obtained from electron transfer oxidation of dT by triplet AQS indicated that the produced radical ion pairs, radical cations of dT and radical anion of AQS, were identified simultaneously.

2. EXPERIMENTAL

2-Anthraquinonesulfonatesodium (AQS) (Fluka, >98%) was recrystallized twice from triply distilled water before use. 2-Deoxythymidine (dT) was purchased from sigma. All the samples were prepared in triply distilled water and deoxygenated by bubbling with high purity nitrogen (99.99%). All experiments were carried at room temperature. Laser flash photolysis experimental methods and the specifications of equipment (KrF excimer laser: 248 nm; pulse wide: 20 ns, 50 mJ) has been described previously [6].

3. RESULTS AND DISCUSSION

3.1. The Characteristic Transient Absorption Spectra of the H-Abstraction Radicals of Deoxyribonucleotide Bases

Figure 1 shows the transient absorption spectra at 1 μs after laser photolysis of N₂ saturate CH₃CN-H₂O (97:3) solution containing 1 × 10⁻⁴ mol·dm⁻³ deoxyribonucleotide bases (TMP, dCMP, dGMP, dAMP) and 2 × 10² mol·dm⁻³ K₂S₂O₈ and 2 × 10⁻² mol·dm⁻³ t-BuOH, respectively. These characterized transient absorption peaks are very similarity that reported previously [5-7],

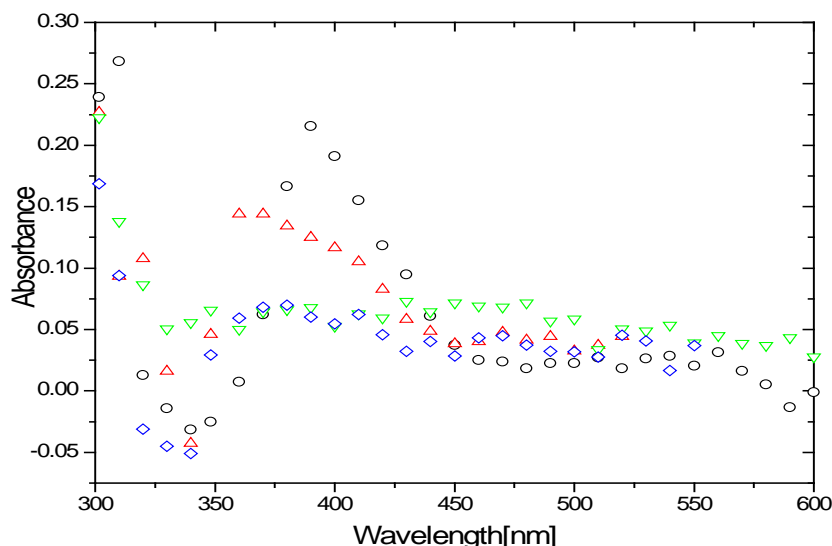
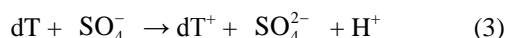
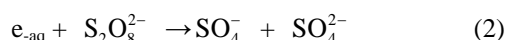


Figure 1. N_2 saturate CH_3CN-H_2O (97:3) solution containing $1 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ deoxyribonucleotide bases (TMP, dCMP, dGMP, dAMP) and $2 \times 10^2 \text{ mol}\cdot\text{dm}^{-3}$ $K_2S_2O_8$ and $2 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$ t-BuOH. (\diamond) TMP, (\blacktriangledown) dCMP, (\triangle) dAMP, (\circ) dGMP, respectively. Recorded at 40 μs after laser excitation.

should be reasonably ascribed to the radical cation of H-abstraction radicals of deoxyribonucleotide bases. It is clear that the same radical cation species were produced in different experiments. For example, the one of generation of dT radical cation can be illustrated as below:



3.2. The Transient Absorption Spectra of the Interaction of AQS with dT

In our present paper, the characteristic transient absorption spectra of radical anion of AQS (AQS^-) and triplet AQS ($^3\text{AQS}^*$) are from laser photolysis in deaerated CH_3CN-H_2O (97:3) solution have been reported, and the spectrum characterized at 510 nm and 380 nm, 470 nm, 580 nm have assigned to radical anion of AQS (AQS^-) and triplet AQS ($^3\text{AQS}^*$), respectively [8].

Figure 2 shows transient absorption spectra from laser photolysis of $0.028 \text{ AQS mmol}\cdot\text{dm}^{-3}$ and $0.05 \text{ mmol}\cdot\text{dm}^{-3}$ dT in CH_3CN-H_2O (97:3) solution, saturated with N_2O . After the pulse, an absorption band characterized at ~ 510 nm and decays by second order kinetics, which is similar to that of the radical anion of AQS reported previously [8], and should be assigned to AQS^- . The late transient absorption characterized rang 350 nm - 450 nm, should be reasonably ascribed to the radical cation of dT-H due to its similarity to that the radical cation of dT in **Figure 1** and photoinization of deoxyribonucleotide [8,9]. The growth trace of transient species at 510 nm was occurred

exactly in the same time interval as did the AQS triplet decay at 580 nm (**Figure 3**), which decayed following first-order kinetics, and it is the net contribution of triplet AQS ($^3\text{AQS}^*$), as shown **Figure 4**.

So we implying that the AQS triplet state is the precursor of the radical anion and transient species at 350 nm - 450 nm, revealing the feature of dT^+ characterized. It is evident that $^3\text{AQS}^*$ was quenched by dT via electron transfer producing long lived dT^+ species.

3.3. The kinetic Parameters of Transient Species and Free Energy Change (ΔG) of Electron Transfer between AQS and dT

In the reaction of electron transfer between AQS and dT, the formation trace of dT^+ at 360 nm can be obtained by subtracting the absorbance at 580 nm multiplied by A^{360}/A^{580} from that at 360 nm. At mean time, the formation trace of AQS^- at 510 nm can be obtained by subtracting the absorbance at 580 nm multiplied by A^{510}/A^{580} from that at 510 nm too. The corresponding kinetic parameters of transient species growth at 360 nm, 510 nm and triplet AQS decay at 580 nm are $1.2 \times 10^9 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, $1.6 \times 10^9 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ and $1.5 \times 10^9 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, respectively. Obviously, the formation rate constants of radical cations of dT and radical anion of AQS are nearly equal to that of decay of triplet AQS respectively. On the other hand, The ΔG (free energy changes) for the electron transfer of between triplet AQS and dT can be calculated according to the Rehm-Weller equation and the E_{ox} values of dT was calculated via an

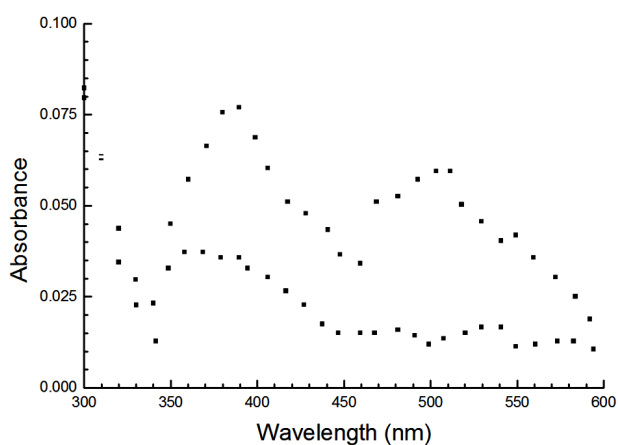


Figure 2. Transient absorption spectra from laser photolysis of $0.028 \text{ mmol}\cdot\text{dm}^{-3}$ AQS and $0.05 \text{ mmol}\cdot\text{dm}^{-3}$ dT in $\text{CH}_3\text{CN}\text{-H}_2\text{O}$ (97:3) solution, saturated with N_2O . (□) $1 \mu\text{s}$, (■) $25 \mu\text{s}$.

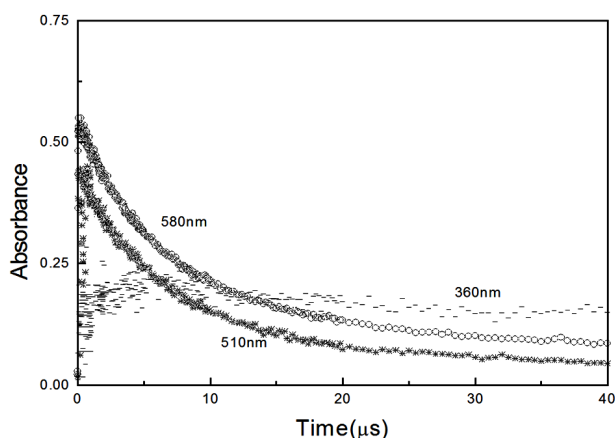


Figure 3. Decay and growth curves of mixed solution of $0.028 \text{ mmol}\cdot\text{dm}^{-3}$ AQS and $0.05 \text{ mmol}\cdot\text{dm}^{-3}$ dT at 580 nm, 510 nm and 360 nm.

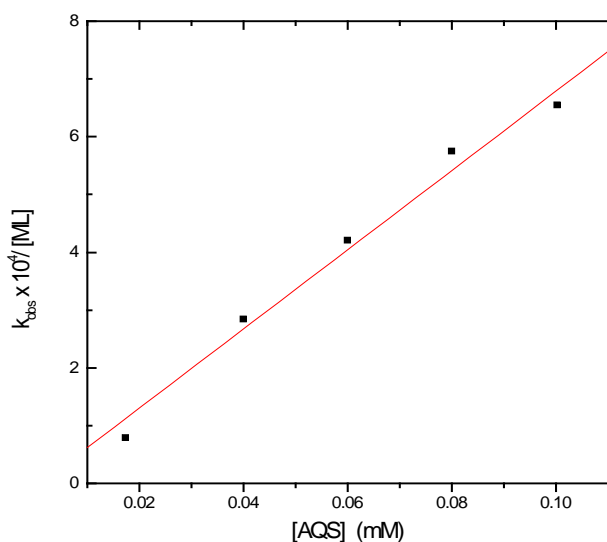
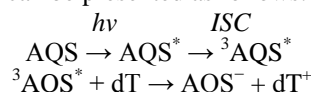


Figure 4. Plot of the apparent decay rate constant of ${}^3\text{AQS}^*$.

empirical equation $E_{\text{ox}} = 0.89\text{IP} - 6.04$ [10], and the E_{red} (AQS, vs. SCE), $\Delta E_{0,0}$, ΔG (energy of ${}^3\text{AQS}^*$), $e^2/\epsilon d$ and the coulombic term are published results [11-14], respectively. From these, free energy change (ΔG) value (KJ/mol) was calculated as $dT-68.3$ KJ/mol. It means that the electron transfer oxidation reactions between triplet AQS and dT is exothermic.

From the above results, these experimental findings provide reliable evidence for the electron transfer oxidation reactions between triplet AQS and dT. The predominant initial species from electron transfer oxidation of dT is dT radical cation. The proposed reaction mechanism of generation of the dT radical cation and the radical anion of AQS can be presented as follows:



4. CONCLUSION

The transient absorption spectra of interaction of triplet AQS with dT were observed and the rate constants for formation of radical cation of dT and those of radical anion of AQS and the decay of triplet AQS were also determined. The time resolved evidence of dynamic and thermo-dynamic of laser spectra and kinetics of radical ion pairs from electron transfer oxidation of dT by triplet AQS were provided.

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