

## Photoinduced Electron Transfer Reaction between Poly-guanylic Acid (5) with Anthraquinone-2-sulfonate

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**Abstract:** The electron transfer reaction between triplet anthraquinone-2-sulfonate with poly-guanylic acid (5) (poly[G]) in acetonitrile-H<sub>2</sub>O has been investigated by 248 nm laser flash photolysis. The transient absorption spectra of radical cation of poly[G] and radical anion of anthraquinone-2-sulfonate (AQS) arising from electron transfer reaction has been observed simultaneously for the first time. The formation processes of radical cation of poly[G] and radical anion of anthraquinone-2-sulfonate as well as the decay processes of triplet anthraquinone-2-sulfonate have also been observed, the apparent rate constants for the formation and decay of transient species have been determined. The free energy changes in the process of the electron transfer was also calculated.

**Keywords:** Electron transfer reaction, poly[G], anthraquinone-2-sulfonate.

The interaction of quinone photonuclease with DNA has been widely studied. Anthraquinone derivatives, in particular that of anthraquinone-2-sulfonate has been used as cleaving agent for duplex DNA<sup>1–5</sup>. However, direct observation of excited ion pairs of biomolecules especially the stabilized radical cation of biomolecule is hampered by the overwhelming transient absorption of hydrogen bonded radical anion of quinone.

In this work, the interaction of poly[G] with triplet anthraquinone-2-sulfonate in CH<sub>3</sub>CN- H<sub>2</sub>O (97:3) *via* electron transfer reaction has been achieved by using laser photolysis techniques. The laser spectra and kinetics of radical ion pairs from electron transfer oxidation of poly[G] by triplet AQS, were reported for the first time.

### Materials and Method

Poly-guanylic acid (poly[G]) was obtained from Sigma. anthraquinone-2-sulfonate (Fluka, > 98 %) was recrystallized twice in triply distilled water before use. CH<sub>3</sub>CN (Chromatographic grade). All samples were prepared in triply distilled water and deaerated by high purity nitrogen (99.99%) bubbling for 20 min. All experiments were carried out at room temperature.

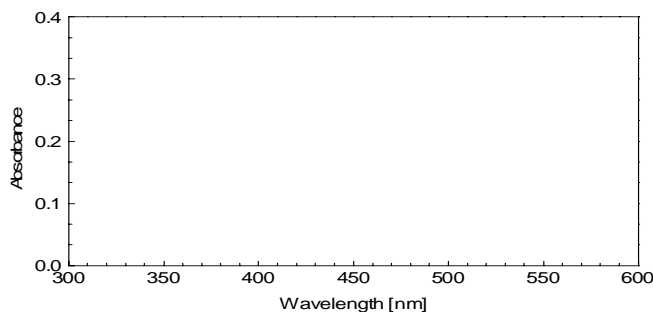
An excimer laser (KrF, 248 nm, 20 ns pulse, ≤50mJ per pulse) was used for sample excitation. The signals were collected using a HP54510B 300MHz transient recorder then processed with a PC-486 computer. Detailed descriptions of the equipment and experimental conditions were given elsewhere<sup>6</sup>.

### Characteristic absorption spectra of the Radical anion of AQS and triplet AQS

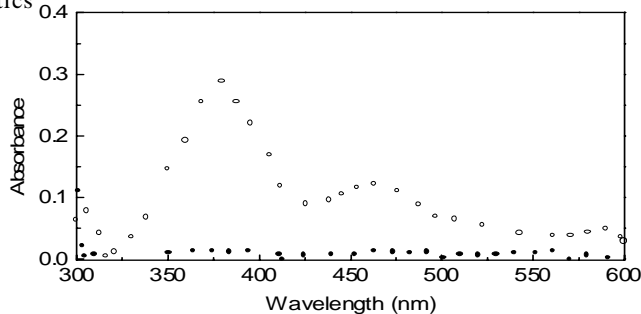
The transient absorption spectrum characterized by  $\lambda_{\max}$  at  $\sim 510$  nm from pulse radiolytically produced radical anion of AQS in  $\text{CH}_3\text{CN}$  (**Figure 1**) and decay by second order kinetics should be assigned to radical anion of AQS, since its transient absorptions are remarkably similar to that of radical anion of AQS reported previously<sup>7</sup>.

The characteristic absorption spectra of the triplet AQS from laser excitation of AQS in deaerated  $\text{CH}_3\text{CN-H}_2\text{O}$  (97:3), as show in **Figure 2**. The spectrum characterized by signals at 380 nm, 470 nm and 580 nm can be quenched by  $\text{Mn}^{+2}$  or  $\text{O}_2$  and decayed following first-order kinetics. Thus, it should be assigned to triplet AQS as described in our previous work<sup>8</sup>.

**Figure 1.** Transient absorption spectra after laser excitation of 0.3mM AQS and 100 mMN $\text{aNO}_3$  in nitrogen saturated  $\text{CH}_3\text{CN-H}_2\text{O}$ (3%) at (●)1 $\mu\text{s}$



**Figure 2** Transient absorption spectra after laser excitation of 0.3 mM AQS in nitrogen saturated  $\text{CH}_3\text{CN-H}_2\text{O}$ (3%) at (o)1 $\mu\text{s}$ , (●)10 $\mu\text{s}$ . Insert: Plot of  $\ln(\text{OD})$  vs. time in the first-order kinetics



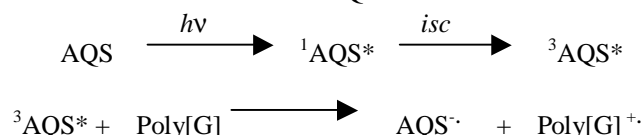
### Interaction of AQS with poly[G]

**Figure 3** shows the transient absorption spectra produced from interaction of AQS with poly[G] recorded at two time delays (1 $\mu\text{s}$ , 40 $\mu\text{s}$ ) after laser excitation. The early spectrum in **Figure 3** with absorption maximum at  $\sim 510$  nm, consistent with the reported spectrum<sup>9</sup>, should also be assigned to  $\text{AQS}^-$  due to its remarkable similarity to that of radical anion produced from laser photolysis of  $\text{NaNO}_2$  in  $\text{CH}_3\text{CN-H}_2\text{O}$ (3%) (**Figure 1**) and photoinization of 2 deoxyguansine by 193 nm light<sup>13</sup>.

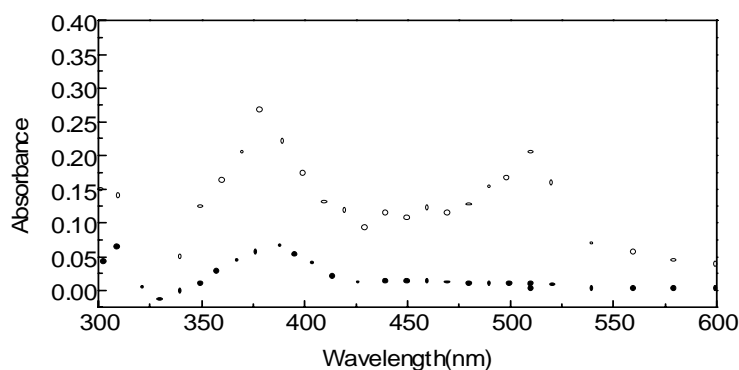
The late spectrum in **Figure 3**, revealing the feature of poly[G] radical cation characterized. with a  $\lambda_{\max}$  at  $\sim 310$  nm and another weak peak at  $\sim 390$  nm, should be reasonably ascribed to poly[G] radical cation, which is essentially similar to that from acetone sensitization, monophotonic ionization of poly[G]<sup>10-12</sup>. By comparison of the early spectra in **Figure 1** and that in **Figure 3**, it is evident that radical anion of AQS is

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the common initial species from interaction of poly[G] with triplet AQS, while the long lived species should be reasonably ascribed to poly[G] radical cation. The generation of the poly[G] radical cation and radical anion of AQS can be illustrated as below :



**Figure 3.** Transient absorption spectra after laser excitation of 0.07mM poly[G] and 0.3mM AQS in nitrogen saturated CH<sub>3</sub>CN-H<sub>2</sub>O(3%) at (o)1μs; (●)40μs

**Determination of the kinetic parameters of the transient species**

From above reaction mechanism, triplet AQS was quenched by poly[G] *via* electron transfer producing poly[G] radical cation and AQS radical anion.

**Figure 4** shows the transient absorption traces from the photolysis of poly[G] in the presence of AQS. The pseudo-first order quenching rate constants of triplet AQS by poly[G] have been determined from the decay trace at 580 nm and the pseudo-first order rate constants for formation of radical cation of poly[G] have also been determined by the growth trace of radical anion 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. It is evident that the growth trace of transient species of radical cation of poly[G] and radical anion of AQS are synchronous with decay of triplet AQS, respectively. The rate constants of formation of radical cation of poly[G] and radical anion of AQS is  $5.3 \times 10^5 \text{ s}^{-1}$ . And  $4.8 \times 10^5 \text{ s}^{-1}$ , the rate constant of decay of triplet AQS is  $5.8 \times 10^5 \text{ s}^{-1}$ .

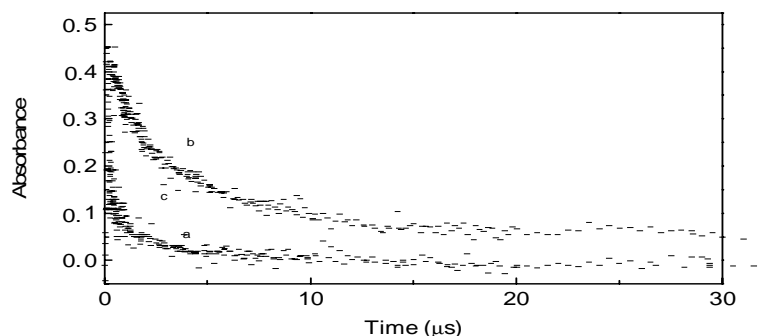
**Calculation of free energy changes ( $\Delta G$ )**

The free energy changes in the process of the electron transfer can be calculated according to the Rehm-Weller equation<sup>14</sup>:

$$\Delta G = 96.48 (E_{\text{ox}} - E_{\text{red}} - e^2 / \epsilon d - \Delta E_{0,0})$$

While  $E_{\text{ox}}$  and  $E_{\text{red}}$  are the half-wave potential in volts for the oxidation of an electron donor and reduction of an electron acceptor, respectively. The  $E_{\text{ox}}$  values (*vs* SCE) of guanine was calculated by an empirical equation  $E_{\text{ox}} = -0.89\text{IP} - 6.04$ <sup>15</sup>. The corresponding IP values was adopted from Nikogosyan<sup>16</sup> for guanine and from Colson et al<sup>17</sup>. The determined  $E_{\text{red}}$  value of AQS is -0.81V (*vs* SCE).  $\Delta E_{0,0}$  (2.68 eV), 0,0 energy of  ${}^3\text{AQS}^*$ <sup>18</sup> ( $\Delta G$ ), and  $e^2 / \epsilon d$  (0.06 eV), the coulombic term, are published results<sup>19</sup>. Thus  $\Delta G$  value (KJ/mol) was obtained as guanine -101.3 kJ/mol. Calculated free energy changes indicate that electron transfer from poly[G] to  ${}^3\text{AQS}^*$  is exothermic.

**Figure 4** Transient absorption growth decay traces obtained by photolysis of 0.07mM poly[G] containing 0.3mM AQS in CH<sub>3</sub>CN-H<sub>2</sub>O(3%) saturated with nitrogen. Trace a. decay at 580 nm; trace b. growth at 510 nm; trace c. growth obtained by subtracting trace a multiplied by  $A^{510} / A^{580}$  from trace c. trace d growth at 310 nm.



### Conclusions

The above results demonstrate directly that the initial species from interaction of AQS with poly[G] ion pairs composed of radical cation of poly[G] and AQS<sup>-</sup> which have provided dynamic evidence for the initiation of electron transfer from poly[G] to triplet AQS producing triplet ion pairs. In addition,  $\Delta G$  value showed that the electron could efficiently transfer from guanine to triplet AQS.

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