Laser photolysis of interaction of poly-guanylic acid (5') with anthraquinone-2-sulfonate

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Abstract The electron transfer reaction between triplet anthraquinone-2-sulfonate and poly-guanylic acid (5’) in CH₃CN-H₂O (97 : 3) has been investigated by 248 nm (KrF) laser flash photolysis. The transient absorption spectra and kinetics obtained from the interaction of triplet anthraquinone-2-sulfonate and poly[G] demonstrate that the primary ionic radical pair, radical cation of poly[G] and radical anion of anthraquinone-2-sulfonate have been detected simultaneously. The free energy changes in the process of the electron transfer were also calculated.

Keywords: anthraquinone-2-sulfonate, poly[G], laser photolysis.

The photophysics and photochemistry of anthraquinone compounds have been studied extensively. Anthraquinone derivatives in particular that of anthraquinone-2-sulfonate (AQS) have been used as cleaving agent for duplex DNA[1–5]. 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 electron transfer reaction between poly[G] and triplet anthraquinone-2-sulfonate in CH₃CN-H₂O (97 : 3) has been achieved. The kinetics of radical ion pairs from electron transfer oxidation of poly[G] by triplet anthraquinone-2-sulfonate, have been determined simultaneously.

1 Experimental

Anthraquinone-2-sulfonate, obtained from Fluka, was recrystallized twice in triply distilled water before use. CH₃CN (chromatographic grade). Poly-guanylic acid (5’) (poly[G]) was obtained from Sigma. 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.

Laser photolysis experiments were performed using a home-made excimer laser which provides a 248 nm (KrF) light pulse with a duration of 20 ns. The maximum laser energy is ≤50 mJ per pulse. The signals were collected using an HP54510B 300 MHz transient recorder then processed with a PC-486 computer. Detailed descriptions of the equipment and experimental condi-
tions were given elsewhere[6].

2 Results and discussion

2.1 Characteristic absorption spectra of the radical anion of anthraquinone-2-sulfonate and triplet anthraquinone-2-sulfonate

As shown in fig.1, transient absorption spectra are observed from laser photolysis of 0.3 mmol/L anthraquinone-2-sulfonate and 100 mmol/L NaNO$_3$ in nitrogen-saturated CH$_3$CN-H$_2$O(3%).

The transient absorption spectrum characterized by $\lambda_{\text{max}}$ at ~510 nm from laser photolysis producing radical anion of anthraquinone-2-sulfonate in CH$_3$CN-H$_2$O(3%) (fig.1) and decayed by the second order kinetics should be assigned to radical anion of anthraquinone-2-sulfonate since its transient absorptions are remarkably similar to that of radical anion of anthraquinone-2-sulfonate reported previously[3,4].

The characteristic absorption spectra of the triplet anthraquinone-2-sulfonate are from laser excitation of anthraquinone-2-sulfonate in deaerated CH$_3$CN-H$_2$O (3%), as shown in fig. 2. The spectrum characterized by signals at 380, 470 and 580 nm can be quenched by Mn$^{2+}$ or O$_2$ and decayed following first-order kinetics. Thus, it should be assigned to triplet anthraquinone-2-sulfonate[3,4].

2.2 Interaction of anthraquinone-2-sulfonate with poly[G]

Fig. 3 shows the transient absorption spectra produced from interaction of anthraquinone-2-sulfonate with poly[G] recorded at two time delays (1 and 40 $\mu$s) after laser excitation. The earlier spectrum in fig. 3 with absorption maximum at ~510 nm, being consistent with the reported spectrum[7], should also be assigned to anthraquinone-2-sulfonate radical anion due to its remarkable similarity to that of radical anion produced from laser photolysis of NaNO$_2$ in CH$_3$CN-H$_2$O (3%) (fig. 1). The later spectrum in fig. 3, with a $\lambda_{\text{max}}$ at ~310 nm and another weak