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Effect of phosphate group in switching off electron transfer in different media

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ABSTRACT

We have studied the interactions of individual nucleoside 5′-monophosphates of all the five nucleic acid bases, adenosine 5′-monophosphate (AMP), guanosine 5′-monophosphate (GMP), thymidine 5′-monophosphate (TMP), cytidine 5′-monophosphate (CMP) and uridine 5′-monophosphate (UMP) with two quinones, 9,10-anthraquinone (AQ) and 2-methyl 1,4-naphthoquinone (MQ) commonly known as menadione using laser flash photolysis in two different types of media. Although electron transfer (ET) in excited state is a well-known phenomenon in DNA with quinones, this work reveals a total failure of ET with these isolated 5′-monophosphate molecules in a homogeneous medium (acetonitrile/water), except GMP. Similar experiments in SDS micelles have been repeated but here even GMP failed to transfer electrons. We have attributed the failure of ET in homogeneous medium to a semi-circular conformation adopted by the 5′-monophosphates, which is assumed to pull back the electrons from the electron donor center, the nitrogenous base. In SDS micelles a rapid spin exchange within an abnormally short inter-radical distance has been considered to prevent ET.

1. Introduction

Electron transfer (ET) and H atom transfer/H abstraction (HA) are already established as two very important modes of reactions in biological systems. ET within DNA has been widely investigated by several eminent scientists [1–7]. It is accepted that charges are transported over long distances through a multistep hopping reaction within DNA [8–10]. Therefore the involvement of nucleotides in ET within DNA has already been established.

Now there are several reports on the isolated monophosphate molecules of nucleic acid bases regarding ET where we can get an idea of both the occurrence and non-occurrence of ET [11–13]. Since the past few years we have been working with the nucleic acid bases and their nucleosides separately with two quinone molecules 2-methyl 1, 4-naphthoquinone, commonly known as menadione (MQ) and 9,10-anthraquinone (AQ) which can be considered as model anticancer drugs [14–23]. Nucleic acid bases and their nucleosides generally serve as electron donors and quinone molecules as electron acceptors in an ET reaction. In the case of hydrogen abstraction (HA) reaction, the former serves as potent H atom donor and again quinones are the acceptors. Both ET and HA have been found to be excited state reactions. In our earlier works we have already established ET to be a favored reaction between AQ, MQ and all the five DNA bases and their corresponding nucleosides, in two contrasting media, a homogeneous one composed of acetonitrile/water (ACN/H_2O, 9:1, v/v) and a heterogeneous micellar medium of sodium dodecyl sulfate (SDS) in water [15–21]. Here we have investigated the mode of interaction of the five monophosphates of the same nucleic acid bases individually with these quinones in similar media to find if the introduction of a single phosphate moiety has to do anything with the dominant ET channel already existing with the bases and the nucleosides. Interestingly, with the monophosphates we have observed ET to get a backseat in the two media. We have tried to find out the reasons behind these phenomena.

Initially we have investigated the interaction of all the five monophosphates with both MQ and AQ in ACN/H_2O where except GMP all the others have failed to exhibit ET. Earlier other researchers had similar observation too [11,12] but the reason remained vague. In our work we have proposed such failure to result from an adoption of a semi-circular conformation by a monophosphate molecule which is just appropriate in pulling back electron density from the electron rich donor site. Since ET is known to be a distance-dependent phenomenon [24], we have repeated similar experiments in SDS micelles with water as solvent to investigate whether closer approach among molecules can switch on ET. SDS micelles are known to entrap molecules in their interior hydrophobic core thus increasing the local concentration of the

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Abbreviations: MQ, 2-methyl 1, 4-naphthoquinone; AQ, 9, 10-anthraquinone; AMP, Adenosine 5′-monophosphate; GMP, Guanosine 5′-monophosphate; TMP, Thymidine 5′-monophosphate; CMP, Cytidine 5′-monophosphate; UMP, Uridine 5′-monophosphate; ISC, Intersystem crossing; MF, Magnetic field; MFE, Magnetic field effect; S, Singlet; T, Triplet; ET, Electron transfer; RP, Radical pair; RIP, Radical ion pair; H, Hydrogen; SDS, Sodium dodecyl sulfate; ACN, Acetonitrile; H_2O, Water; J, Exchange interaction.

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molecules by bringing them close together and also restricting the free movement of the molecules. We have applied an external magnetic field (MF) in our experiments in micelles, which plays a crucial role as a supporting evidence for the proper identification of the reaction intermediates with their initial spin states formed out of several possibilities [15–21,25–27]. Now ET or HA produces radical ion pairs or radical pairs (RIPs/RPs), the generation of which can be ascertained from MFE [15–21].

In the initially formed geminate RPs/RIPs the conversion between singlet (S) and triplet ($T_{\pm}$, T_0) spin states takes place by electron–nuclear hyperfine interaction [25–27] present in the system. An external MF removes the degeneracy of the $T_{\pm}$ with S and T_0 thereby reducing the ISC. The overall effect is the increase in the population of the initial spin state, which is reflected in an increase in the absorbance of the transients (radicals or radical ions) initially produced in triplet spin state in our case. Therefore MFE also helps in identification of the exact intermediates (RPs/RIPs) with their spin states.

Our studies have revealed some interesting observations. Initially we have used ACN/H_2O (9:1, v/v) as the reaction medium where only GMP has exhibited ET to both MQ and AQ. Next, in an effort to bring molecules closer we have repeated similar experiments in SDS. Even then no ET has been discerned with others and surprisingly, ET has stopped from GMP also. Application of MF in SDS has shown a very small increase in absorbance. A substantial increase indicates presence of triplet RPs/RIPs of appreciable lifetime but such nominal increase can only be attributed to a rare occurrence of spin exchange among monophosphates and quinones. Thus we have concluded that the addition of an extra phosphate group to the nucleosides has played a crucial role by preventing ET which has been the usual route even with the nucleosides, the cause being different in the two different media.

2. Experimental

2.1. Materials

Menadione (MQ), adenosine 5′-monophosphate (AMP), guanosine 5′-monophosphate (GMP), thymidine 5′-monophosphate (TMP), cytidine 5′-monophosphate (CMP) and uridine 5′-monophosphate (UMP) and sodium dodecyl sulfate (SDS) were purchased from Sigma. 9,10-Anthraquinone (AQ) was obtained from Aldrich and was recrystallized from ethanol. UV spectroscopy grade acetonitrile (ACN) was obtained from Spectrochem and used without further purification. Water used for preparation of solutions was triply distilled. All micellar solutions were made by sonication. Chemical structures of the compounds used in this work are shown in Chart 1.

2.2. Spectral methods

The absorption spectra were measured by a Thermospectronic absorption spectrophotometer (model UNICAM UV 500). Transient absorption spectra are measured using nanosecond flash photolysis set-up (Applied Photophysics) containing an Nd:YAG laser (DCR-II, Spectra Physics). The sample is excited by 355 nm laser light (FWHM = 8 ns). The analyzing light is from a 250 W Xenon lamp. The laser and analyzing light beams, crossed at right angles, passed through a quartz cell with 1 cm^2 cross-section. A monochromator equipped with an IP28 photo-multiplier is used to analyze transient absorption (Applied Photophysics). The signals from the photo-multiplier are displayed and recorded as a function of time on a Tektronix 500 MHz (1Gs/s sampling rate) oscilloscope, TDS 3054B and the data has been transferred to a computer using TekVISA software. Each data point has been obtained with multi-times average to improve the signal-to-noise ratio. The transient absorption spectra are obtained from a series of oscilloscope traces measured with the same solution in a point-by-point manner with respect to the wavelength using the software Origin 7.5. The samples have been deaerated by passing pure Argon gas for 20 min prior to each experiment. No degradation of the samples has been observed during the experiments. The MF effect (0.08 T) on the transient spectra has been studied by passing direct current through a pair of electromagnetic coils placed inside the sample chamber.

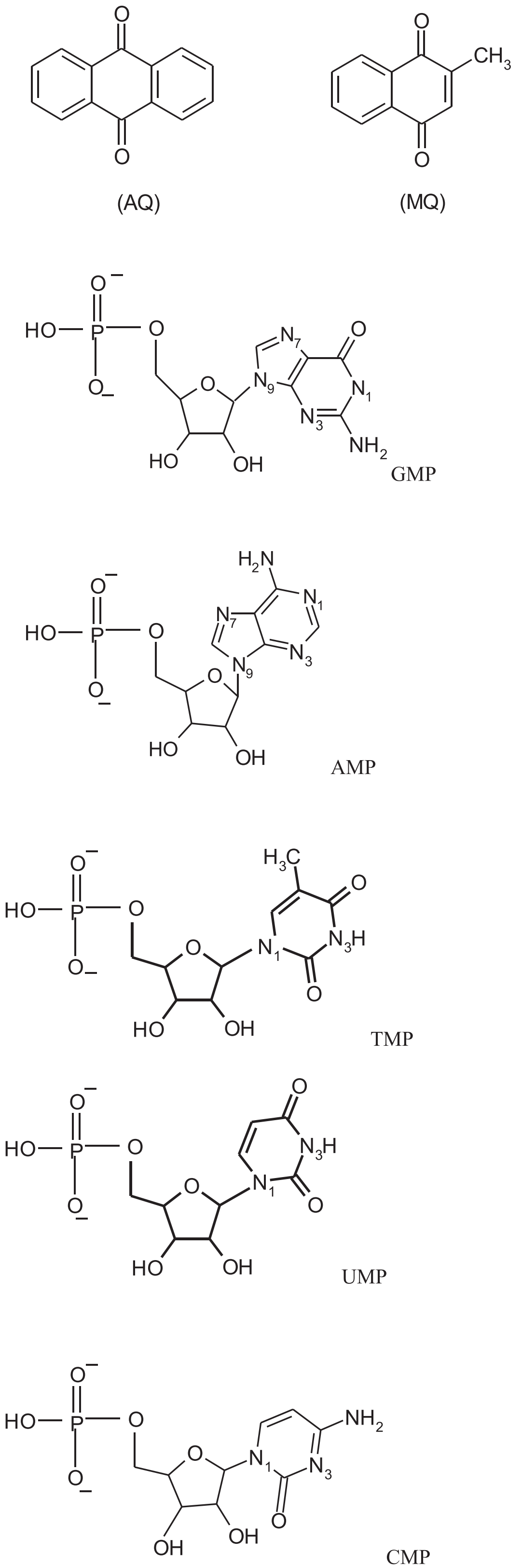

Chart 1. Molecular structures of AQ, MQ, AMP, GMP, TMP, UMP and CMP.