Laser Flash Photolysis and Magnetic Field Effect Studies on the Interaction of Uracil and Its Derivatives with Menadione and 9,10-Anthraquinone

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Laser flash photolysis and an external magnetic field have been used to study the interaction of two quinone molecules, namely, 9,10-anthraquinone (AQ) and 2-methyl-1,4-naphthoquinone, commonly known as menadione (MQ), with the RNA base uracil (U) and two of its derivatives, 1,3-dimethyluracil (dmU) and uridine (dU). We have conducted our studies in homogeneous organic and heterogeneous micellar media in order to investigate the effect of media on the molecules and any change in reactivity on account of substitution. In organic homogeneous medium, both the quinones have behaved similarly with the bases. Here U has undergone both electron transfer (ET) and hydrogen (H) transfer, while dU and dmU have failed to exhibit any ET. Failure to support ET has been attributed to keto−enol tautomerism, which has been found to have a significant role in determining the occurrence of ET from these pyrimidine bases. However, in SDS micelles some variations regarding the reactivity of these molecules have been discerned. The variations are 2-fold. Here ET from U has been found to get completely eclipsed by a dominant H abstraction with both the quinones, and AQ reveals a difference in the extent of H abstraction with the bases in SDS. With U and dU, the prevailing H abstraction with AQ has succeeded in formation of only $AQH^{\bullet}$, while dmU has produced both $AQH^{\bullet}$ and AQH_2, the latter being formed by two successive H abstraction. Explanations of this intriguing behavior with U and its derivatives with quinone molecules have been the main concern in this work.

1. Introduction

Quinones are ubiquitous in nature. In photosynthetic and respiratory electron transfer chains, the quinones play a relevant role as mediators of vectorial electron and proton transport. Nowadays quinones are the second largest family of anticancer drugs clinically used in the United States[1] because of their role as toxicological intermediates that can create a variety of hazardous effects in vivo, including acute cytotoxicity, immunotoxicity and carcinogenesis.[2] The quinone molecules are localized within the biological membrane, where they form a freely diffusing "pool" component. Surfactant micelles are the simplest equivalent of biological membranes; therefore, they are frequently employed to mimic the biological aggregates. Hence, studying quinone molecules within micelles and then comparing the results with that in homogeneous medium can be useful in obtaining insight into the reaction mechanisms and changes, if any, with different biomolecules. We are currently investigating the mode of interactions of two important quinones, menadione (2-methyl-1,4-naphthoquinone, MQ) and 9,10-anthraquinone (AQ), which are potential models for anticancer drugs,[3,4] with all the nucleic acid bases and their nucleosides individually.[5−7] Electron transfer (ET) between quinones and DNA has been established to be an important reaction. Eminent scientists like Schuster, Barton, Wagner, and several others have contributed significantly in this field.[8−14] In this work, we have aimed at elucidating the photochemical behavior of the bases with the quinones right from the initiation of their interactions, in two different categories of media, an organic 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. Our main focus is to detect any change in the reactivity of these molecules on changing their immediate surroundings. Homogeneous medium allows the reactants to be randomly distributed while the micelles formed by surfactant molecules serve as simple membrane mimetic systems that allow a controlled study of the effect of confined medium on the interaction of different molecules. Our earlier works with adenine, thymine, guanine, and their nucleosides revealed alterations in their reactivity in the above-mentioned pair of media.[5−7] We hope our studies on the medium dependence of reactivity of nucleic acid bases will prove beneficial in understanding the effect of environment on the action of a potential drug with biological molecules. In this regard, we have studied the interaction of MQ and AQ with RNA bases, uracil (U) and two of its derivatives, 1,3-dimethyl uracil (dmU) and uridine (dU), in the above-mentioned media. In this work, we have attempted to investigate the mode of interactions of the quinone molecules with the bases and to find any changes in reactivity brought about by the effect of substitution on U in different media. We have utilized the laser flash photolysis photolysis technique with an associated magnetic field (MF), only in micellar medium, for our studies. We have explained the courses of their reactions, which have been undergoing alteration on changing reaction media.

We have observed two very different reactions, ET and hydrogen (H) abstraction occurring between U, dU, and quinones. As further support for the occurrence of ET/H abstraction with the bases, we have employed an external MF, which has the potential of correctly identifying the different intermediates formed during the reaction in SDS. ET and H abstraction reactions lead to the formation of radical ion pairs (RIPs)/radical pairs (RPs), which contain unpaired electrons and in general can be affected by an external magnetic field (MF).[15−23] The magnetic field effect (MFE) arises due to competition between

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electron spin dynamics and radical separation. The geminate RPs/RIPs have either singlet or triplet spin configurations. The application of an external MF results in Zeeman splitting of the triplet sublevels, which in turn slows down the intersystem crossing (ISC) process, thereby increasing the population of the initial spin state. It should be mentioned here that for triplet-derived RPs/RIPs the use of a heterogeneous micellar medium is necessary to observe MFE effects by prolonging the lifetime of RPs/RIPs such that they can retain their geminate character for a sufficiently long time for spin flipping to occur.[15] So for a triplet-generated RP, an external MF can increase the triplet population and hence increase radical escape. This is reflected in an increased absorbance on application of MF. Thus, the MF can perturb the free radical concentration in a system. This has immense significance in free-radical-based biochemical reactions. MFE has immense potential in identifying the transients formed during reaction, which in turn is useful in the proper elucidation of reaction mechanism. Our system reveals interesting differences in the extent of ET and H abstractions within the above-mentioned media. MFE has been utilized for the first time with these bases in understanding their reaction pattern.

Reaction Scheme and the Spin-Dependent Phenomenon: The reaction scheme of the present system is as follows:

$$Q \xrightarrow{h\nu} {}^1Q^* \xrightarrow{ISC} {}^3Q^* \quad (1)$$

$${}^3Q^* + RH(SDS) \rightarrow {}^3(Q^{\bullet\bullet}HR) \quad \text{(H abstraction)} \quad (2)$$

$${}^3(QH^{\bullet\bullet}R) \underset{MF}{\overset{HFI}{\longleftrightarrow}} {}^1(QH^{\bullet\bullet}R) \quad (3)$$

$${}^3(QH^{\bullet\bullet}R) \rightarrow QH^{\bullet} + R^{\bullet} \quad \text{(escape product)} \quad (4)$$

$${}^1(QH^{\bullet\bullet}R) \rightarrow QH{-}R \quad \text{(cage product)} \quad (5)$$

$${}^3Q^* + D \rightarrow {}^3(Q^{\bullet-}D^{\bullet+}) \quad \text{(electron transfer)} \quad (6)$$

$${}^3(Q^{\bullet-}D^{\bullet+}) \underset{MF}{\overset{HFI}{\longleftrightarrow}} {}^1(Q^{\bullet-}D^{\bullet+}) \quad (7)$$

$${}^3(Q^{\bullet-}D^{\bullet+}) \rightarrow Q^{\bullet-} + D^{\bullet+} \quad \text{(escape product)} \quad (8)$$

The following steps of reactions are for hydrogen abstraction in the case of U/dU/dmU with quinones:

$${}^3Q^* + D \rightarrow {}^3[QH^{\bullet\bullet}D(-H)] \quad \text{(H abstraction)} \quad (9)$$

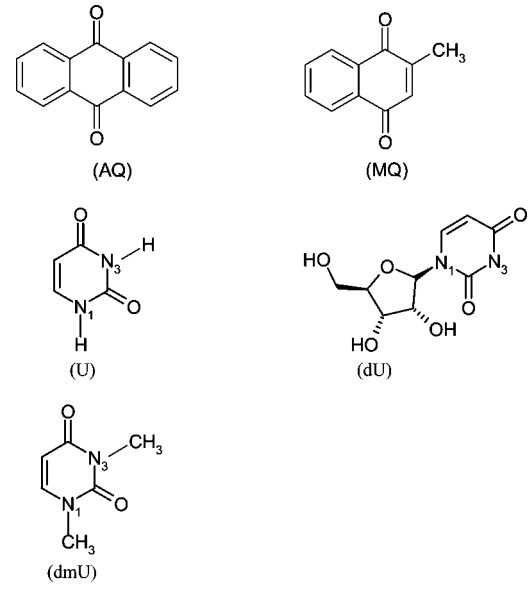
$${}^3[QH^{\bullet\bullet}D(-H)] \underset{MF}{\overset{HFI}{\longleftrightarrow}} {}^1[QH^{\bullet\bullet}D(-H)] \quad (10)$$

Here Q represents quinone molecules, D represents base molecules (U/dU/dmU), and HFI denotes hyperfine interaction. The excited triplet state of quinone, $^3Q^*$, is produced via the excited singlet state through ISC. It abstracts a hydrogen atom from a SDS (RH) molecule (or any suitable H donor) to produce a spin-correlated RP in the triplet state, $^3(QH^{\bullet\bullet}R)$, which consists of a semiquinone and a dehydrogenated SDS radical. The ISC from the triplet pair $^3(QH^{\bullet\bullet}R)$ to the singlet pair $^1(QH^{\bullet\bullet}R)$ and the escape of component radicals into free radicals take place competitively. The singlet geminate RPs disappear due to cage reaction and the triplet one decays by diffusion of the radicals out of the micelle. Similar phenomena occur during ET.

2. Experimental Section

2.1. Materials. MQ, U, dmU, dU, and SDS were purchased from Sigma. AQ was obtained from Aldrich and was recrystallized from ethanol. UV spectroscopy grade 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 molecules used in this work are shown in Chart 1.

CHART 1: Structures of Compounds Used



2.2. Spectral Methods. Transient absorption spectra were measured using a nanosecond flash photolysis setup (Applied Photophysics) containing an Nd:YAG laser (DCR-II, Spectra Physics). The sample was excited by 355 nm laser light (fwhm = 8 ns). The analyzing light was 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 photomultiplier was used to analyze transient absorption (Applied Photophysics). The signals from the photomultiplier were displayed and recorded as a function of time on a Tektronix 500 MHz (1 Gs/s sampling rate) oscilloscope (TDS 3054B), and the data were transferred to a computer using TekVISA software. Each data point was obtained with multitimes average to improve the signal-to-noise ratio. The transient absorption was 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 5.0. The samples were deaerated by passing pure argon gas for 20 min prior to each experiment. No degradation of the samples was observed during the experiments. The MF effect (0.08 T) on the transient spectra was studied by passing direct current through a pair of electromagnetic coils placed inside the sample chamber.

3. Results and Discussion

3.1. Interaction of U, dU, and dmU with MQ. The transient optical absorption spectra obtained on irradiating 0.4 mM MQ separately and in presence of pyrimidine base U (5 mM) and its corresponding nucleoside dU (5 mM) dissolved in ACN/H_2O (9:1, v/v) 1 μs after laser flash at 355 nm are shown in Figure 1. Irradiation of MQ alone generates a peak around 370 nm (curve 1), which has been assigned to triplet−triplet absorption of ^{3}MQ.[5,24] The 355 nm laser light is capable of exciting quinones only and not the nucleic acid bases, since the absorption bands of the latter lie around 300 nm.[25,26] Addition of U (curve 2) has resulted in a sharp increase in intensity with a peak around 370 nm. The region around 500

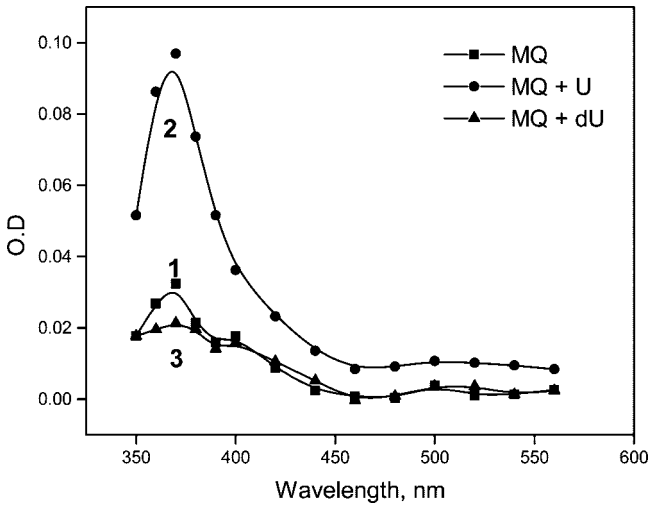


Figure 1. Transient absorption spectra of (1) MQ (0.4 mM) (■), (2) MQ (0.4 mM)−U (5.0 mM) (●), and (3) MQ (0.4 mM)−dU (5.0 mM) (▲) at 1.0 μs time delay after laser pulse with excitation wavelength 355 nm in ACN/H_2O (9:1, v/v).

TABLE 1: λ_{max} of Different RPs/RIPs

species	λ_{max} (nm)	second peak (nm)
$MQH^{\bullet}$	370	~410
$MQ^{\bullet-}$	390	480
$U^{\bullet+}$	390	500
$(U–H)^{\bullet}$	~420	
$AQH^{\bullet}$	370	
AQH_2	460	
$AQ^{\bullet-}$	~400	520

TABLE 2: Variation of Decay Rate Constant (k_f) with Magnetic Field for Aqueous Micellar Solution (SDS) of MQ and the Bases

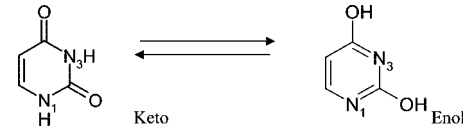
base	magnetic field (T)	decay rate constant, k_f $(s)^{-1}$
no base	0.00	4.17×10^6 (±0.02)
	0.08	1.66×10^6 (±0.01)
U	0.00	5.26×10^6 (±0.03)
	0.08	1.85×10^6 (±0.05)
dU	0.00	5.24×10^6 (±0.03)
	0.08	2.27×10^6 (±0.01)
dmU	0.00	5.84×10^6 (±0.03)
	0.08	2.70×10^6 (±0.01)

nm possesses appreciable absorption, too. The increased absorption at 370 nm may apparently seem to be due to increased yield of ^3MQ upon energy transfer from U. But energy transfer is reported to be very unlikely between quinones and DNA bases.[27,28] So a second possibility can be ET. In our earlier works[5,24] we mentioned that upon ET, MQ serves as an electron acceptor and generates the radical anion $MQ^{\bullet-}$, which absorbs around 380 and 480 nm. We have also reported that, upon irradiation, if H abstraction occurs from a suitable H atom donor molecule, a semiquinone $MQH^{\bullet}$ is formed, which absorbs around 370 nm with a hump at 410 nm. The credibility of ET between MQ and U is enhanced by simultaneous observation of the radical cation of U ($U^{\bullet+}$). It is reported that $U^{\bullet+}$ absorbs around 390 nm with a second peak at 500 nm.[29] Now we have noticed a drastic change in the nature of the spectrum upon addition of U to MQ in the wavelength region scanned. Having knowledge about the peak positions of RPs/RIPs, it seems evident that such behavior can only be associated with a predominant ET between U and MQ. Table 1 displays the λ_{max} values of the different radicals formed. Now the presence of $MQH^{\bullet}$ cannot be neglected totally: first, because it absorbs at 370 nm and, second, because

TABLE 3: Variation of Decay Rate Constant (k_f) with Magnetic Field for Aqueous Micellar Solution (SDS) of AQ and the Bases

base	magnetic field (T)	decay rate constant, k_f $(s)^{-1}$
no base	0.00	3.15×10^6 (±0.02)
	0.08	1.26×10^6 (±0.01)
U	0.00	5.58×10^6 (±0.03)
	0.08	3.73×10^6 (±0.05)
dU	0.00	4.09×10^6 (±0.03)
	0.08	2.20×10^6 (±0.01)
dmU	0.00	4.59×10^6 (±0.03)
	0.08	2.25×10^6 (±0.01)

SCHEME 1: Keto−Enol Tautomerism of Uracil



uracil possesses acidic hydrogen atoms that are reported to undergo a facile deprotonation.[30,31] The formation of $MQH^{\bullet}$ is actually not a very favored reaction mode in ACN/H_2O, as molecules are randomly distributed in such a homogeneous medium due to their incessant motion. A hydrogen bonding type interaction is assumed to precede H abstraction, and incessant motion in homogeneous medium generally does not allow such H bonding. So the formation of $MQH^{\bullet}$ will be possible only if the intrinsic H-donating capacity of H donor molecule is very strong,[5−7,32,33] which is the case with the base uracil. The behavior of the nucleoside dU with MQ is represented in curve 3. The region from 370 to 500 nm is quenched. $MQ^{\bullet-}$ is reported to possess a high value of molar extinction coefficient,[34] so its presence is always marked by an increased absorbance around 380 and 480 nm. But dU has failed to satisfy this criterion. Hence, the absence of RIPs, $MQ^{\bullet-}$, and $dU^{\bullet+}$ is confirmed. This can be attributed to a failure of dU to participate in ET and also a lower probability of H abstraction with MQ. Concentration of $MQH^{\bullet}$ is definitely much less, which is responsible for such low absorbance at 370 nm. Uracil and uridine differ from each other by an additional sugar moiety in the latter, so logically, the reduced interaction of dU with MQ should stem from this difference in structure. A closer analysis of their structure (Chart 1) provides a suitable explanation. We already know that acidic hydrogen atoms of U readily deprotonate,[30,31] so dU, with the N1 acidic hydrogen replaced by a sugar group, exhibits a fall in H abstraction, as expected. Some H abstraction is possible from N3 of dU. A decrease in the number of acidic hydrogen atoms decreases the probability of H abstraction also. Again, dU has exhibited a negligible ET in comparison to U. Now we think that this can also be linked to the sugar moiety. A fall in ET in the case of dU is inevitably associated with a fall in electron density in the molecule, so dU is definitely electron-deficient in comparison to U. This can only be explained by considering keto−enol tautomerism between U and its derivatives, since keto−enol tautomerism is reported to have a significant effect on the chemistry of pyrimidines.[35−39] Scheme 1 depicts the tautomerism possible in U. The enol form of U possesses a benzenoid structure with an aromatic sextet of electrons. A benzenoid nucleus, on account of aromaticity, possesses higher electron density than a nonbenzeniod one.[40] So the enol form is expected to be more prone toward ET than the keto form. Slobadan et al. had reported that U in its enol form is more readily oxidized.[41] Hence ET, which is basically one-electron oxidation, will be more favored in U.[5] Similar reasoning cannot be applied for dU, where the sugar moiety

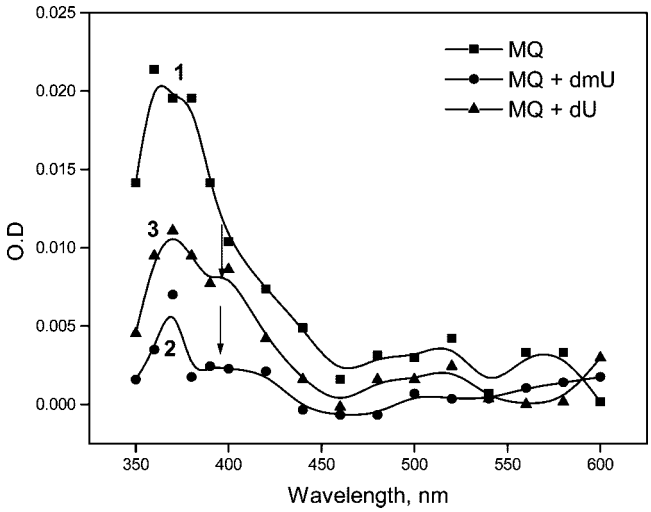


Figure 2. Transient absorption spectra of (1) MQ (0.4 mM) (■), (2) MQ (0.4 mM)−dmU (5.0 mM) (●), and (3) MQ (0.4 mM)−dU (5.0 mM) (▲) at 1.0 μs time delay after laser pulse with excitation wavelength 355 nm in ACN/H_2O (9:1, v/v).

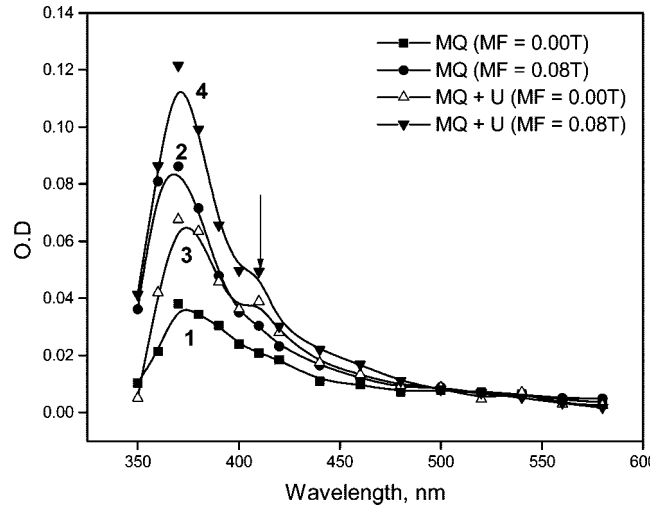


Figure 3. Transient absorption spectra of MQ (0.4 mM) in (1) the absence (■) and (2) the presence (●) of magnetic field and MQ (0.4 mM)−U (5.0 mM) in (3) the absence (Δ) and (4) the presence (▼) of magnetic field at a delay of 1.0 μs in SDS micelles.

inhibits tautomerism (including N1), which thus inhibits the attainment of aromaticity. Again the sugar moiety present in dU can also exert suitable field effect in solution[40] to withdraw electrons away from the base unit due to its electronegative oxygen atoms. Steenken had also reported the role of electronegative oxygen atoms of the sugar unit in pulling away electron density from the base unit.[42] These factors render dU electron-deficient. Thus, the fall in ET and H abstraction on going from U to dU could be justified according to the above understanding.

Hydrogen linked to N atoms in U and dU is reported to be involved in H atom transfer because of its intrinsic acidity.[30,31] If we can replace these acidic hydrogen atoms, a further reduction in H atom transfer is expected. Thus, we have taken 1,3-dimethyluracil (dmU), where two methyl groups replace both N1 and N3 hydrogen atoms. Figure 2 depicts the transient absorption spectra of MQ in the presence of dmU and dU. It is noticed that both dmU and dU exhibit a sharp fall in intensity through out the wavelength range scanned. This points to a quenching of ^{3}MQ by both dmU and dU. But a closer analysis of the nature of the peaks at 350−400 nm reveals some differences between curves 2 and 3 and curve 1. Both curves 2 and 3 possess a broad shoulder around 400 nm, which is not seen in curve 1 due to ^{3}MQ absorption. Our earlier reports point to a semiquinone, $MQH^{\bullet}$, formation with the 400 nm shoulder.[5,33] Thus, a weak H abstraction is found to be the only mode of interaction of dmU and dU. The possibility of ET is almost negligible, since then the presence of $MQ^{\bullet-}$ and radical cation from dmU would have resulted in significant absorptions around 390 and 480 nm, which is not the case. Again the peak height of dU is higher than that of dmU, which is also in accordance with our expectation. In dU, only the N1 acidic hydrogen is removed, but the N3 acidic hydrogen is present, which can undergo facile deprotonation. But in dmU, both N1 and N3 hydrogen atoms are replaced, thus devoiding the molecule of its acidic protons. Now the sugar moiety is reported to undergo some H abstraction[43−46] and the methyl groups have the potential to donate their H, too,[47,48] so a very weak H abstraction from dmU in ACN/H_2O has been discerned. An interesting feature is observed in connection with the behavior of U and dmU. A drastic quenching of ET is noticed in dmU in ACN/H_2O, so it is evident that introduction of two methyl groups at N1 and N3 reduces both ET and H abstraction. The decrease in H abstraction has already been attributed to the absence of acidic hydrogen atoms. The presence of methyl groups could not augment H abstraction in ACN/H_2O, but the decrease in ET in dmU apparently seems contradictory, because methyl groups are known to exert a positive inductive effect,[40,49] which can push electrons toward the ring. So dmU should have exhibited a better ET than U. Hence, the reverse behavior of the molecules is an indication of some opposing effect, which has played the controlling role. Considering the keto−enol tautomerism phenomenon again, it is evident that an aromatic nucleus (enol form) is achieved only by U. Failure of dmU to enolize is thus the major reason for its failure to transfer electrons. Hence, a study of U and its derivatives has proved that tautomerism is one of the significant factors in determining the behavior of these molecules pertaining to ET. In our earlier works,[5,6,24] we have reported that a change in medium from ACN/H_2O to SDS can alter the reaction pathways from a dominant ET to H abstraction with small amine bases, adenine, guanine, and their nucleosides, as SDS has an inherent capability of increasing H abstraction by increasing the local concentration of the reactants.[5,6,24] So we have again performed similar experiments in a caged/restricted environment, as in SDS micellar medium, where the molecules are prevented from separating away from each other to find whether the change in environment can affect the reactivity of uracil and its derivatives toward quinones.

Figure 3 depicts the transient absorption spectra due to MQ alone and MQ with U in SDS. For the experiments in SDS, we have utilized an external MF for the determination of the exact intermediates out of several possibilities with the reactants. We have already mentioned before that MF provides 2-fold information. The increase in absorbance on application of MF proves (i) the existence of radicals and (ii) a triplet spin state of reaction. Here curve 1 reveals the spectra due to irradiation of MQ alone in SDS, while curve 2 depicts the effect produced by MF on the irradiated MQ. Application of MF has resulted in an increase in the 370 nm peak, marking the presence of a radical species. This 370 nm peak has already been attributed to the presence of semiquinone radical, $MQH^{\bullet}$ [5,24] generated upon H abstraction of MQ from a nearby SDS molecule on laser flash (reaction 2).[5,33] Now addition of U has resulted in a further increase in the 370 nm peak with a shoulder around 420 nm (curve 3). The region around 500 nm is totally devoid of any MFE, which

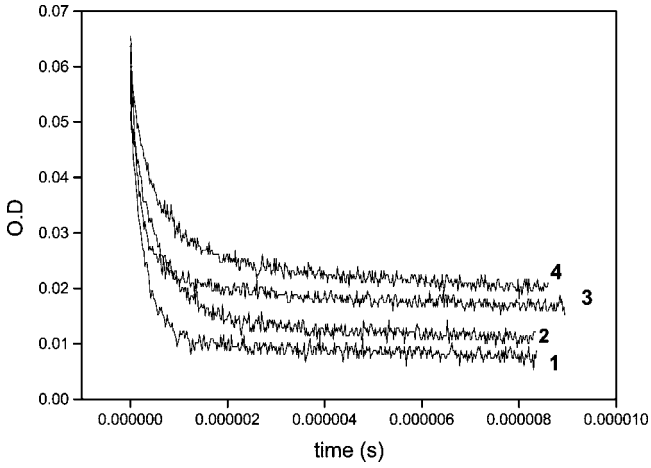


Figure 4. Normalized OD traces at 380 nm obtained by laser flash photolysis ($\lambda = 355$ nm) of MQ (0.4 mM) in SDS in (1) the absence and (2) the presence of a magnetic field and MQ (0.4 mM) and U (5.0 mM) in (3) the absence and (4) the presence of a magnetic field.

thus nullifies the existence of radical ions, which can be formed upon ET (refer to Table 1). Thus, with the help of MF, existence of only $MQH^{\bullet}$ could be discerned, so ET, which has been the dominant reaction mode in homogeneous medium from U, is seen to be completely or almost completely quenched in SDS. Application of MF (curve 4) has resulted in an increase around 370 and 420 nm. Now on comparing all the curves, the shoulder at 420 nm is found to be less pronounced in the case of MQ alone. This can be due to two reasons. First, U has promoted a better H abstraction than MQ, so the ~420 nm shoulder is more pronounced. A second possibility may be that the ~420 nm shoulder indicates the existence of uranyl radical $U(-H)^{\bullet}$, which is formed after H atom transfer from U. Formation of $U(-H)^{\bullet}$ is reported by some authors,[50,51] but to the best of our knowledge, its assignment has not been determined so far.

$$^3MQ^* + U \rightarrow {}^3[MQH^{\bullet\bullet}U(-H)] \quad \text{(H atom transfer)}$$

Figure 4 depicts the magnetic field effect on the decay profile of MQ in the absence and presence of U in SDS. In the presence of an external magnetic field, the decay of the transient at 380 nm becomes slower (Figure 4) accompanied by an enhanced absorption in the spectrum (Figure 3). The formation of a spin correlated radical pair ($^3MQH^{\bullet\bullet}R$) (reaction 2) explains this MFE (reaction 3). It is noteworthy that the nature of the decay profiles (at 380 nm) of $MQH^{\bullet}$ is similar in the presence of U. This implies that the RPs formed with U are also similar with that of MQ alone, that is, $MQH^{\bullet}$ only.

In the presence of an external magnetic field, the decay of the radical pair is expected to be biexponential;[52] i.e., the following equation is obeyed for the change in absorbance, $A(t)$

$$A(t) = I_f \exp(-k_f t) + I_s \exp(-k_s t)$$

where k_f and k_s are the respective rate constants for the fast and slow components of the decay profiles. The fast components of this equation correspond to the radical pair decay in the micellar cage, while the slower one is due to the reaction of the escaped radicals. The k_f values obtained by biexponential fitting of the decay profiles for MQ with all the three bases are listed in Table 2. It is observed that, with increasing field, the decay rate decreases. This implies that the RIPs are generated in the triplet spin state. Upon application of a magnetic field, the conversion of the triplet RIP to the singlet RIP is retarded, and consequently, the decay rates are decreased.

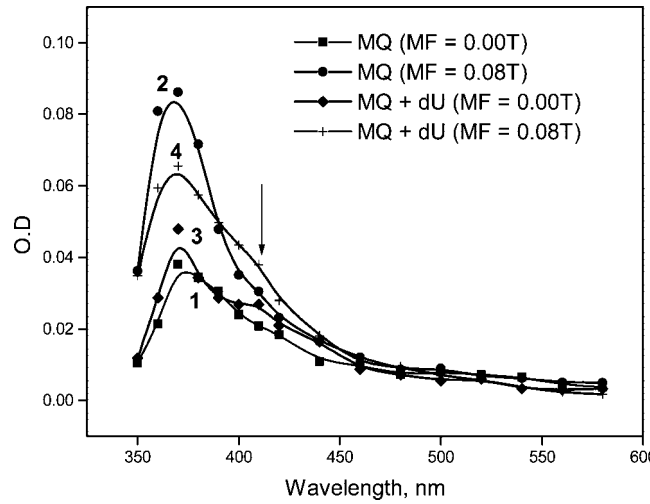


Figure 5. Transient absorption spectra of MQ (0.4 mM) in (1) the absence (■) and (2) the presence (●) of magnetic field and MQ (0.4 mM)−dU (5.0 mM) in (3) the absence (◆) and (4) the presence (+) of magnetic field at a delay of 1.0 μs in SDS micelles.

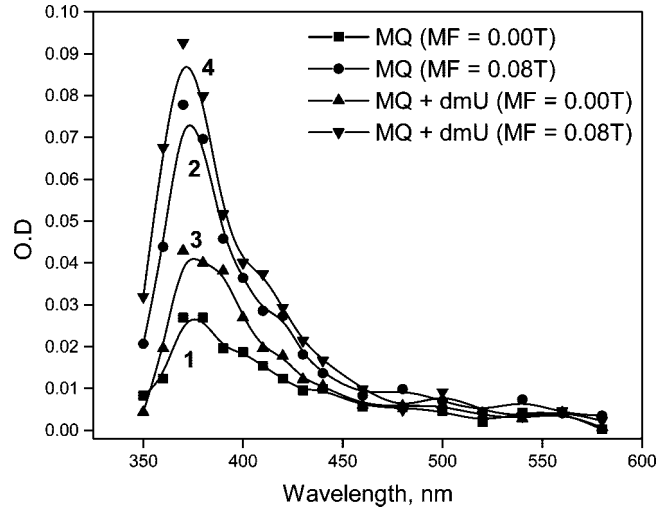


Figure 6. Transient absorption spectra of MQ (0.4 mM) in (1) the absence (■) and (2) the presence (●) of magnetic field and MQ (0.4 mM)−dmU (5.0 mM) in (3) the absence (▲) and (4) the presence (▼) of magnetic field at a delay of 1.0 μs in SDS micelles.

Next we proceeded to see the effect of micellar medium on dU and dmU. Figure 5 reveals the spectra obtained on laser flash of MQ in presence of dU. Addition of dU has resulted in a very small increase around 370 and ~420 nm, which are found to exhibit an appreciable MFE, so existence of $MQH^{\bullet}$ and $U(-H)^{\bullet}$ is again obvious, but with a much decreased rate than that with U. We have noticed that the change in medium has resulted in dU having a peak height above that of MQ, and the application of field has resulted in an increase in the peak height. Again dU possesses a broad shoulder around 420 nm, not found in MQ alone, so H atom transfer from dU to MQ producing geminate $MQH^{\bullet}$ and $U(-H)^{\bullet}$ are found to be enhanced in SDS. Thus, we see that change in medium has altered the reactivity of U only, in quenching the occurrence of predominant ET in ACN/H_2O to a predominant H abstraction in SDS. For dU, there has been only an increase in the H abstraction channel. Analysis of similar decay profile curves as in Figure 4 has been further helpful in an understanding of a sole H abstraction in the case of dU with MQ (graph not shown). Figure 6 reveals the absorption spectra of MQ in the presence of dmU in SDS. Observations are almost similar to that of dU, so both dmU

and dU are found to undergo a better H atom transfer to MQ in SDS than that in ACN/H_2O. Thus, we have observed that a change in medium has resulted in a predominance of H atom transfer from all three bases. There has been a switching over of reaction in the case of U from ET to H abstraction in SDS. This is because SDS has an intrinsic tendency to entrap molecules in its hydrophobic interior. Nowick et al. emphasizes that introduction of molecules within micelles in aqueous solution results in better hydrogen bonding between them, as these molecules get shielded from hydrogen bonds from water.[53] We have reported earlier[5,6,24,32,33] that SDS medium promotes H atom transfer on account of close sequestering of participant molecules, which leads to an initial hydrogen-bonding-type interaction and a resultant H atom transfer from donor to acceptor molecules. This type of interaction is weaker in homogeneous organic medium, where due to random distribution chances of proximity between reactants at a particular time are rare. Thus, ET becomes the dominating pathway with or without H abstraction, depending on the nature of the reacting species. On changing medium, the reactants get entrapped and are thus forced to remain in close proximity with each other. Now U is capable of undergoing extensive H bonding,[54] so it is possible that U, in any of its tautomeric form, gets H bonded with MQ. The H abstraction is presumed to be preceded by an H-bonding-type interaction, so an increase in H bonding will evidently increase H abstraction. Thus, a change in medium from organic homogeneous to micellar heterogeneous brings the two molecules closer, which encourages H bonding, hence resulting in a predominant H abstraction. This H bonding is also possible in dU and dmU, and coupled with an increased number of hydrogen-donating centers, dU and dmU undergo better H abstraction in SDS than ACN/H_2O. The presence of acidic protons in U and dU has resulted in some H abstraction in ACN/H_2O by virtue of random uptake of the acidic protons, but since molecules remain widely dispersed in ACN/H_2O, H abstraction from dmU and dU is much weaker than from U. In ACN/H_2O, H abstraction is solely dependent on the acidity of available H atoms.

Surprisingly, ET is found to be almost quenched in the case of U in SDS, whereas, it had been the dominant reaction channel in ACN/H_2O. An occurrence of ET depends primarily on redox potential values of participating molecules[55] and also on the ionization energy (IE) of the electron donor.[56−58] The factors that are important to provide an accurate description of DNA ionization energy in aqueous solution include solvation by water molecules also. The solvent can control the stabilization component of the IE with respect to solute−solvent interactions.[59] Uracil possesses the highest IE among all nucleic acid bases,[60] so the probability of its participation in ET should be low. But again hydration is reported to decrease the IE of U.[61] Now in ACN/H_2O, hydration of water-soluble U is possible, which leads to a reduction in its IE, so a facile ET is achieved. But in SDS, U will get trapped along with quinones[62,63] in the hydrophobic region, so hydration is diminished. Hence, quenching of ET in SDS can be attributed to the absence of hydration and thus a failure of reduction of IE. A study of redox potential values of nucleic acid bases also reveals a high value for uracil, which also points to ET to be a less favorable reaction of U.[41] The same group had also reported that 1-methyluracil possesses an even higher value, so we can logically expect dmU to possess the highest redox potential. Thus, the absence of ET from dmU in both the media and the switching over of the reactivity of U on medium change can be explained. Quinone moieties can be efficiently H bonded with pyrimidines as reported by McCarthy et al.[64] Keto and enol forms of U possess two good hydrogen donor sites, so it can also H bond with the quinone moiety of MQ. In SDS, due to (i) restricted mobility and (ii) close proximity among molecules, scope of H abstraction is always higher, as already discussed. So micellar environment gives preference to H abstraction so much so that, ET faces a strong competition and as our observation reveals, effectively it gets completely quenched.

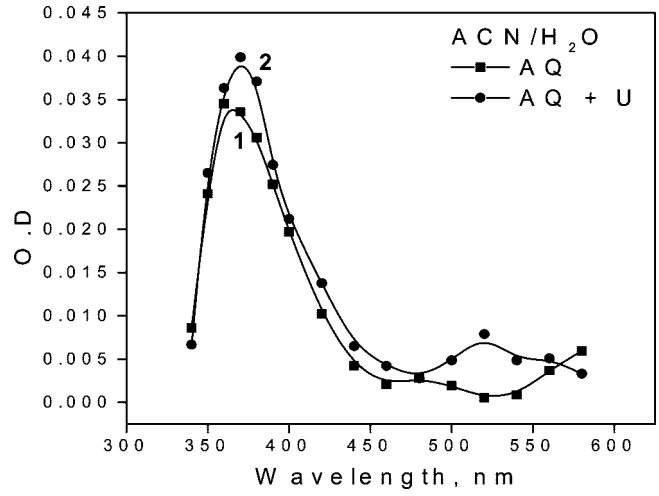


Figure 7. Transient absorption spectra of (1) AQ (0.4 mM) (■) and (2) AQ (0.4 mM)−U (5.0 mM) (●) at 1.0 μs time delay after laser pulse with excitation wavelength 355 nm in ACN/H_2O (9:1, v/v).

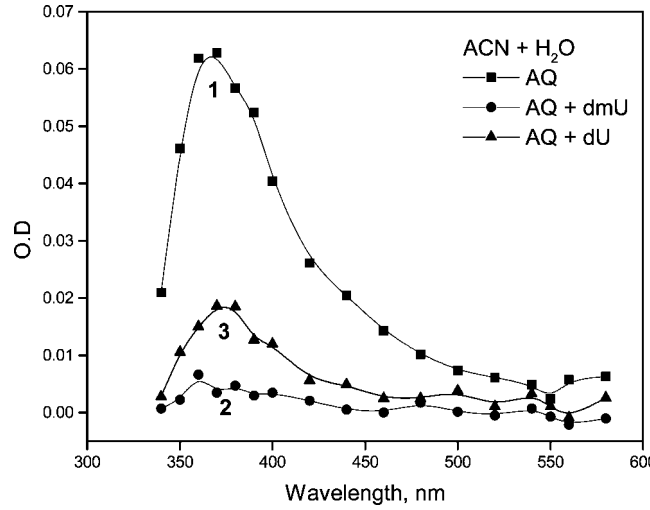


Figure 8. Transient absorption spectra of (1) AQ (0.4 mM) (■), (2) AQ (0.4 mM)−dmU (5.0 mM) (●), and (3) AQ (0.4 mM)−dU (5.0 mM) (▲) at 1.0 μs time delay after laser pulse with excitation wavelength 355 nm in ACN/H_2O (9:1, v/v).

3.2. Interaction of U, dU, and dmU with AQ. In order to find the differences, if they exist, in the behavior of these RNA bases with different size of quinones, we have repeated similar experiments with the higher homologue, AQ. AQ has been observed to behave similarly as MQ with the bases in ACN/H_2O. Figure 7 displays transient absorption spectra upon irradiation of a 0.4 mM AQ solution separately and in the presence of 5 mM of U after 1 μs of laser flash in ACN/H_2O (9:1, v/v), while Figure 8 depicts AQ with dU and dmU in the same medium. In both the figures, AQ alone presents strong maximum around 360 nm, which is due to triplet absorption of ^{3}AQ.[5,6,30] Addition of U (curve 2, Figure 7) has generated a maximum at 370 nm with a second peak around 520 nm. Now in our earlier works we have reported AQH$^\bullet$, formed through

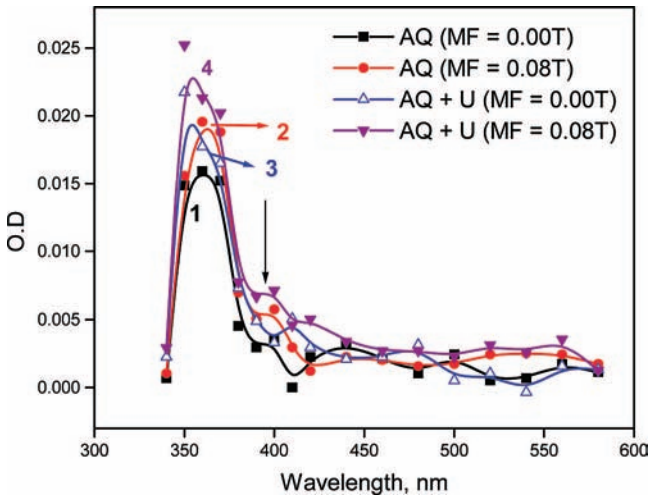


Figure 9. Transient absorption spectra of AQ (0.1 mM) in (1) the absence (■) and (2) the presence (●) of magnetic field and AQ (0.1 mM)−U (5.0 mM) in (3) the absence (Δ) and (4) the presence (▼) of magnetic field at a delay of 1.0 μs in SDS micelles.

H atom transfer from U, to absorb around 370 nm and $AQ^{\bullet-}$, formed through ET, to absorb around 380 and ~520 nm[5,6,30] (Table 1), so observation of peaks corresponding to RIPs confirms the feasibility of ET from U to AQ. From Figure 8, we find dU and dmU to generate small peaks, which can only be attributed to $AQH^{\bullet}$, since the region above 500 nm is devoid of any peaks corresponding to $AQ^{\bullet-}$. Hence in ACN/H_2O, all the three pyrimidine bases have behaved similarly, irrespective of the quinone structure.

Behavior of AQ in micellar medium has been found to be somewhat different from our earlier observations with small organic amine bases.[32] Figure 9 displays the transient absorption spectra obtained on irradiating AQ separately and in presence of U (5 mM) in SDS in presence of an external MF. AQ alone has presented a sharp peak at 370 nm (curve 1) that has undergone appreciable MFE (curve 2), thus pointing toward the geminate behavior of the RPs formed. This 370 nm peak indicates formation of $AQH^{\bullet}$ formed upon H abstraction by AQ from a SDS molecule. Addition of U has resulted in a further increment of this 370 nm peak with a very small shoulder around 420 nm. Both these 370 and 420 nm peaks have exhibited appreciable MFE. Hence, the presence of $AQH^{\bullet}$ and $U(-H)^{\bullet}$ are confirmed in SDS, thus confirming a dominant H atom transfer to be the only mode of reaction between AQ and U. Figure 10 depicts the decay profile curve for AQ−U interaction. Similar observations of almost identical decay profiles for AQ alone and for AQ−U have been obtained here, too, so the sole presence of $AQH^{\bullet}$ has been confirmed. Figure 11 depicts the behavior of dU with AQ. There is absolutely no difference between the behavior of U and dU. Hence, H abstraction is again seen to be the only mode of reaction with dU. Figure 12 displays the transient absorption spectra obtained on irradiating AQ separately and in the presence of dmU (5 mM) in SDS in presence of an external MF. Addition of dmU has generated peaks at 370 and 460 nm, the latter being attributed to the presence of a nonradical species AQH_2, formed upon two simultaneous H atom transfers to AQ[6,32] as follows:

$$^3AQ^* + H^{\bullet} \rightarrow AQH^{\bullet}$$

$$AQH^{\bullet} + H^{\bullet} \rightarrow AQH_2$$

The region 460 nm, due to AQH_2, is seen to be devoid of any MFE. Actually, AQH_2 is formed upon two successive H

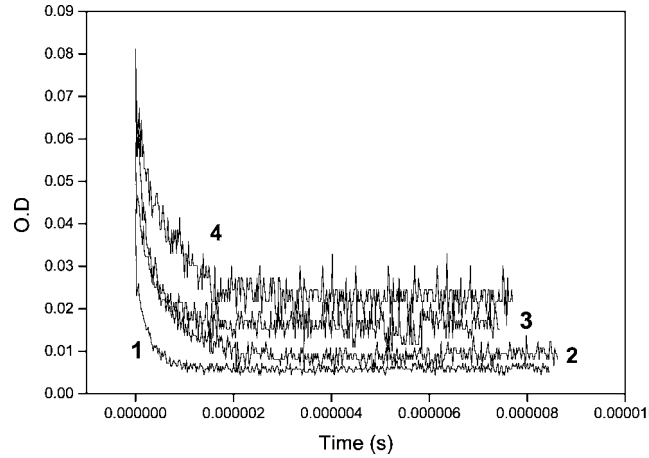


Figure 10. Normalized OD traces at 380 nm obtained by laser flash photolysis (λ = 355 nm) of AQ (0.4 mM) in SDS in (1) the absence and (2) the presence of magnetic field and AQ (0.4 mM) and U (5.0 mM) in (3) the absence and (4) the presence of magnetic field.

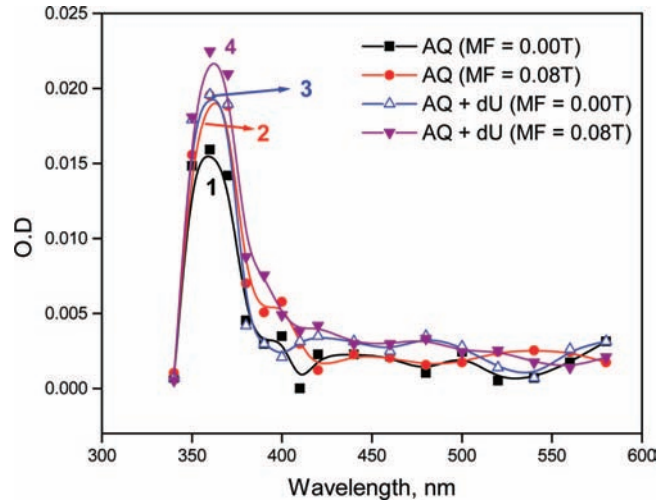


Figure 11. Transient absorption spectra of AQ (0.1 mM) in (1) the absence (■) and (2) the presence (●) of magnetic field and AQ (0.1 mM)−dU (5.0 mM) in (3) the absence (Δ) and (4) the presence (▼) of magnetic field at a delay of 1.0 μs in SDS micelles.

atom transfers. The time required for its formation is sufficient to destroy the geminate behavior of AQ and dmU, so after $AQH^{\bullet}$ formation, further H is no more abstracted from the neighboring dmU only, rather the second H is now abstracted from either SDS or other dmU molecules at a distance. The breakdown of the geminate character between AQ and dmU is responsible for the absence of MFE. In our earlier works with small organic amine bases, a dominant H atom transfer in SDS had always generated both $AQH^{\bullet}$ and AQH_2.[32] But interestingly, in the case of U and dU, this AQH_2 peak has not been observed. On the other hand, dmU has generated AQH_2. This can only be explained by considering a weaker H atom transfer from U and dU to AQ and a comparatively stronger one from dmU. We think that the explanation for this unique behavior lies in the chemical structure of the RNA bases and AQ. H atom transfer is intuitively taken to be preceded by H-bonding-type interaction between the participating molecules. If this H-bonding-type interaction is impeded somehow, transfer of H atom will be disturbed too. Thus, in ACN/H_2O medium, where molecules have more freedom of movement, H abstraction has been a side reaction, whereas in SDS, due to the close proximity of the molecules, it becomes the predominant mode of reaction, so much so that it may often quench a possible ET reaction between

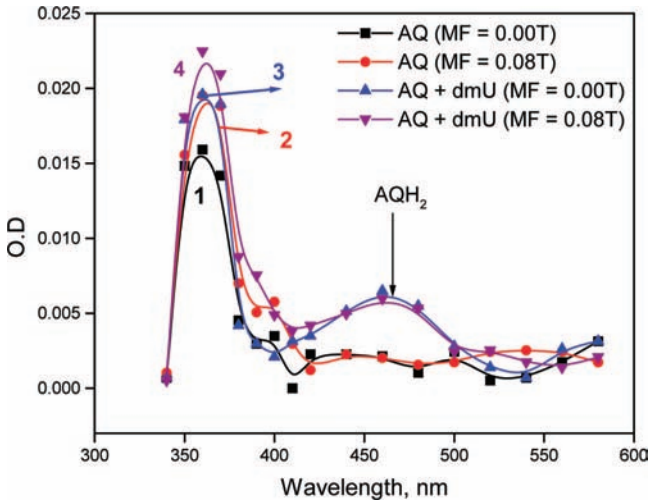


Figure 12. Transient absorption spectra of AQ (0.1 mM) in (1) the absence (■) and (2) the presence (●) of magnetic field and AQ (0.1 mM)−dmU (5.0 mM) in (3) the absence (▲) and (4) the presence (▼) of magnetic field at a delay of 1.0 μs in SDS micelles.

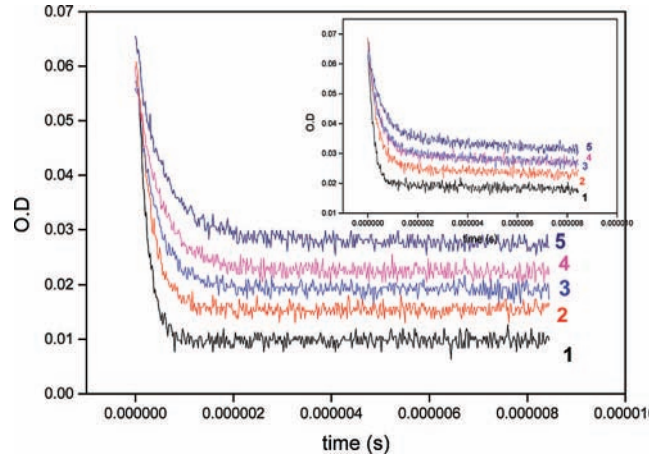


Figure 13. Normalized OD traces at 380 nm obtained by laser flash photolysis of MQ (0.4 mM)−U (5 mM) in SDS at different magnetic fields of (1) 0.005 T, (2) 0.02 T, (3) 0.04 T, (4) 0.06 T, and (5) 0.08 T. Inset: Normalized OD traces at 380 nm obtained by laser flash photolysis of MQ (0.4 mM)−dU (5 mM) in SDS at different magnetic fields of (1) 0.005 T, (2) 0.02 T, (3) 0.04 T, (4) 0.06 T, and (5) 0.08 T.

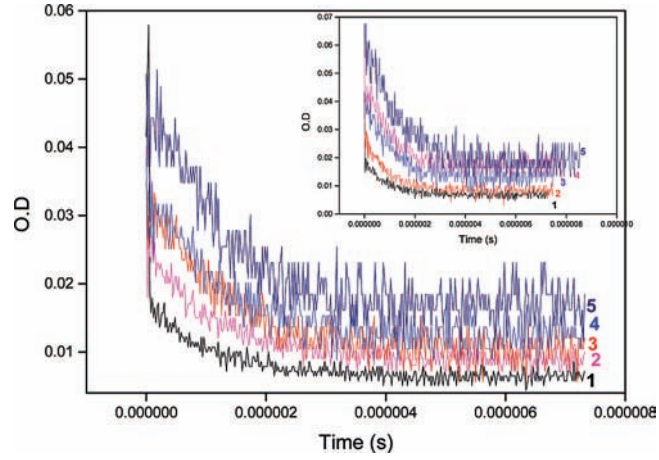


Figure 14. Normalized OD traces at 380 nm obtained by laser flash photolysis of AQ (0.4 mM)−U (5 mM) in SDS at different magnetic fields of (1) 0.005 T, (2) 0.02 T, (3) 0.04 T, (4) 0.06 T, and (5) 0.08 T. Inset: Normalized OD traces at 380 nm obtained by laser flash photolysis of AQ (0.4 mM)−dU (5 mM) in SDS at different magnetic fields of (1) 0.005 T, (2) 0.02 T, (3) 0.04 T, (4) 0.06 T, and (5) 0.08 T.

the same pair of molecules, as had been the case with U and MQ. Our earlier studies with adenosine also gave similar results.[33] Now AQ possesses an additional phenyl moiety than MQ, so in effect, the H acceptor quinone moiety gets shielded from the approach of the H donor DNA bases. Thus, U can transfer its H to AQ with some difficulty, which is manifested in generation of only AQH$^{\bullet}$. Again, dU being larger than U, inspite of more H donor centers, sufficient approach to AQ is highly impeded; thus, again AQH_2 formation is not possible. But, in case of dmU, a compromise is achieved. The size of dmU is less than that of dU, while there is more H donors due to the presence of two methyl groups. We think this situation is ideal for better H atom transfer in SDS; hence, dmU succeeds in generating AQH_2 simultaneously with AQH$^{\bullet}$. Thus, although apparently AQ has behaved similarly as MQ in ACN/H_2O, differences due to a size effect has been evident in SDS.

In order to gain some further information regarding the behavior of the bases with the quinones, we have performed a magnetic field variation experiment for the uracil derivatives using both MQ and AQ. A variation of magnetic field strength can provide information pertaining to the presence of different intermediates. If the trend of the decay profile is compared between two sets of data, a similar trend will reflect the presence of similar species. Figure 13 depicts the magnetic field variation for MQ and Figure 14 depicts that for AQ. In Figure 13, a comparison of MQ-U interaction is shown at 380 nm, while in the corresponding inset, variation for MQ−dU is shown. In both cases of MQ−U and MQ−dU interactions, no significant differences have been found between the decay patterns. This suggests that the transients from U and dU in SDS are similar. Almost similar observations are found with dmU (graph not shown). Figure 14 shows the comparative behavior of AQ−U and AQ−dU. A cursory glance shows that even here there is no difference between the decay patterns, so the presence of semiquinone as the only predominant species in SDS is confirmed.

In this context it is necessary to mention the difference in the H-donating capability among U, dU, and dmU. One acidic proton of U being replaced in dU and two in dmU have resulted in a drop in H abstraction in ACN/H_2O. Now H atom transfer is considered to be preceded by a H-bonding-type interaction between participating molecules if they are close enough. Again, if there is higher concentration of H atoms in medium, it can be suitably abstracted by acceptors. The protons of N1 and N3 of U are appreciably acidic, which results in a high concentration of H atoms (or protons) in medium, so H atom transfer from U is always a favored reaction mode. While dU possesses a single acidic H, dmU possesses none. Our observation reveals that the H atoms of the sugar and methyl moieties of dU and dmU are weakly abstracted by quinones in ACN/H_2O due to their lower acidity, which is responsible for the feeble H abstration in ACN/H_2O. However, on the other hand, entrapment of molecules in micellar core brings them close enough, thus increasing the local concentration of the molecules. This helps in establishing the H-bonding-type interaction between quinones and dU or dmU, which is responsible for the observation of H abstraction from these bases in SDS. Thus, we can infer that by manipulation of reaction medium, it is possible to enhance the rate of a particular reaction that is otherwise unfavorable.

Conclusion

This work reveals the behavior of two quinones, MQ and AQ, with the RNA base U and its derivatives dmU and dU in two types of media. In heterogeneous SDS medium, molecules are closely sequestered in the hydrophobic tails, while in homogeneous medium, they have more freedom of movement. Change in medium has been found to have a marked effect on the chemistry of the bases. While U has been undergoing ET in ACN/H_2O, shifting in SDS has resulted in an almost quenching of ET. There has been a switch over of reaction from ET to a predominant H abstraction in SDS for U. The derivatives dmU and dU completely failed to support ET in both media. An unfavorable redox potential and also failure to attain aromaticity by virtue of keto−enol tautomerism are found responsible for it. Hence, in ACN/H_2O their interaction with quinones is not significant, but in a confined SDS medium, both dU and dmU have been found to transfer H atoms to the acceptor quinone. In a caged environment, a H-bonding interaction between participating molecules is followed by H abstraction. The higher acidity of H atoms of U yields a high concentration of H atoms/protons in medium, which favors H abstraction reaction from U in both the media, but dU possesses a single acidic H, while dmU possesses none, which is reflected in the feeble H abstraction in ACN/H_2O. On the other hand, in SDS, this H abstraction becomes the dominant mode, the explanation of which lies in the increase in the local concentration of the molecules in SDS, which in turn encourages H abstraction from sugar and methyl moieties of dU and dmU, respectively. Lastly, a comparison of MQ and AQ revealed some difference pertaining to their behavior in SDS. The extent of H atom transfer from U and dU to AQ is found to be less than MQ, while dmU is found to undergo appreciable H transfer. This has been attributed to the size difference among the quinones, which plays a crucial role in determining the extent of reaction.

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