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Structure-dependent switchover of reaction modes: A laser flash photolysis and magnetic field effect study

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Abstract

This work illustrates a switchover of reaction mode on account of steric effect in different types of media. We have observed that in polar organic medium, 2-methyl-1,4-naphthoquinone (menadione, MQ) undergoes electron transfer (ET) with different amines, e.g., triethylamine (TEA), *N*,*N*-dimethylaniline (DMA) and 4,4′-bis(dimethylamino)diphenylmethane (DMDPM), whereas in SDS micelles it abstracts hydrogen from DMA and DMDPM although ET persists with TEA. On the contrary, our previous reports indicate that the mode of interaction of 9,10-anthraquinone with DMA and DMDPM is predominantly ET in both these media. Here we have attempted to explain such anomalous behavior.

Keywords: 2-Methyl-1,4-naphthoquinone; Triethylamine; *N*,*N*-Dimethylaniline; 4,4′-bis(Dimethylamino)diphenylmethane; Laser flash photolysis

1. Introduction

Semiquinone radicals derived from naphthoquinone derivatives are implicated for their antitumor action and associated toxic effects [1]. We have intended to study the mode of interaction of one such derivative, 2-methyl-1,4-naphthoquinone (menadione, MQ), a model for quinone drugs used in cancer therapy, with some important amine bases, *N*,*N*-dimethylaniline (DMA), 4,4′-bis(dimethylamino)diphenylmethane (DMDPM) and triethylamine (TEA). It is known that human leukemic cells exposed to MQ suffer from extensive DNA damage [2]. Therefore we felt that it might be worth trying to elucidate the exact nature of interaction of MQ in solution utilizing different important donor molecules. Much work on MQ has been done in aqueous solution [3–5], organic media [6] and micelles [7]. Some have been done in our laboratory regarding the mode of interaction of MQ with DNA bases in acetonitrile (MeCN), a polar organic homogeneous medium and in heterogeneous micellar medium (sodium dodecyl sulphate, SDS). This work reveals a predominance of ET in MeCN and hydrogen (H) atom transfer in micelles [8]. Earlier we had studied the mode of interactions of 9,10-anthraquinone (AQ), a molecule with an additional phenyl ring in comparison to MQ, in same pair of media with DMA and DMDPM and observed a predominance of ET in both the media [9]. This differential behavior indicates that structure of molecules and solvent play an important role in dictating the mode of reaction.

An associated magnetic field effect (MFE) was utilized in SDS micelles to have a better understanding for such differential mode of interactions. An external MFE is possible where two radicals, generated in a particular spin state at a certain distance make a round trip excursion to a distance where exchange interaction is small. An external magnetic field (MF) or the internal MF provided by magnetic nuclei might effect the spin evolution process in between re-encounter and may thus influence the recombination rate. Micelles often increase the MFE on geminate recombination by confining the radical pairs (RPs) and altering the round-trip diffusive excursion path of the two radicals [10–12]. In the absence of a MF, hyperfine interaction (HFI) of the electron with the nucleus can cause the RP singlet state S_0 to evolve into each of the three triplet states (T_0, T_+, T_-) and vice versa. The low MF lifts the degeneracy above the level of the HFI, suppresses the reversible interconversion of S_0 into two

Abbreviations: ET, electron transfer; MQ, 2-methyl-1,4-naphthoquinone or menadione; TEA, triethylamine; DMA, *N*,*N*-dimethylaniline; DMDPM, 4,4′-bis(dimethylamino)diphenylmethane; MeCN, acetonitrile; SDS, sodium dodecyl sulphate; H, hydrogen; AQ, 9,10-anthraquinone; MF, magnetic field; MFE, magnetic field effect; RP, radical pair; RIP, radical ion pair; HFI, hyperfine interaction

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of the triplets ($T_{\pm}$) and thus effects the steady-state distribution of singlet and triplet RPs [10–12]. The overall effect of application of an external MF is an increase in triplet yield if the RPs are formed initially in the triplet state, and decrease in triplet yield or rather an increase in singlet yield if the initial formation is in the singlet state.

In this work our main emphasis has been laid upon the comparison of the different behavior of MQ with aromatic and aliphatic amine bases in polar homogeneous organic media on one hand and heterogeneous micellar media on the other. By using simple laser flash photolysis technique and an associated magnetic field, we have revealed qualitatively the switchover of reaction pattern on mere introduction of an extra phenyl ring on the acceptor MQ that produces its higher homologue AQ while keeping the bases similar and vice versa.

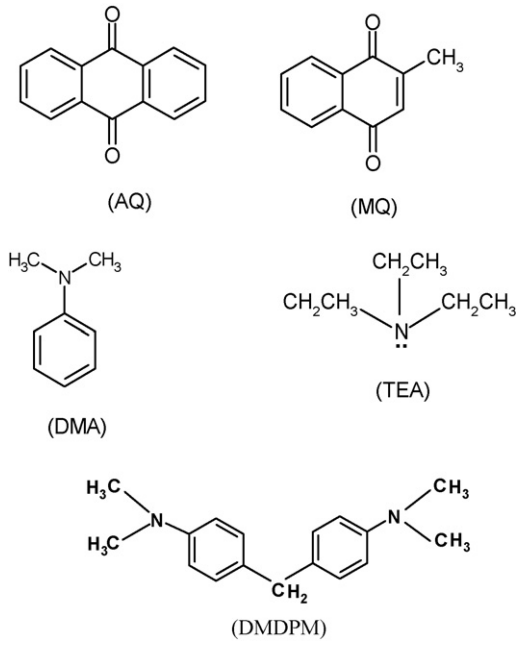
2. Experimental

2.1. Materials

MQ and SDS were purchased from Sigma. DMA and TEA were obtained from Sisco Research Laboratories and Merck, respectively, and both were used after proper distillation. DMDPM was purchased from Aldrich and was recrystallized from ethanol. UV spectroscopy grade MeCN was obtained from Spectrochem and used without further purification. Water was triply distilled. Chemical structures of the acceptors and donors used in this work are shown in Scheme 1.

2.2. Spectral methods

Transient absorption spectra were measured using nanosecond laser flash photolysis set-up (Applied Photophysics) containing an Nd:YAG laser (DCR-11, Spectra Physics). The sample was excited by 355 nm laser light. The details of this set-up have been published earlier [9]. The strength of the magnetic field used was 0.08 T.



Scheme 1.

3. Results and discussion

3.1. Laser flash photolysis: acetonitrile medium

The transient absorption spectrum from photolysis of 0.2 mM deoxygenated MQ solution in MeCN alone at 1.0 μs time delay after laser pulse is shown in Fig. 1. There is a strong absorption maximum at 370 nm with lifetime of 0.8 μs. The 370 nm peak can be assigned to the absorption due to ^{3}MQ [6,8]. Moreover, a small hump around 490 nm is observed (Fig. 1) with similar lifetime of 0.8 μs, therefore both the peaks around 370 and 490 nm is assigned to ^{3}MQ [5]. Inset of Fig. 1 depicts the transient absorption spectra of MQ (0.2 mM) in isopropanol. The peak due to ^{3}MQ absorption, 370 nm, remains unaltered but an additional hump around 420 nm can be discerned. This hump is assigned to MQH$^{\bullet}$ [8], which is generated on H abstraction from isopropanol containing labile H atom [13].

On addition of 0.5 mM TEA, DMA and DMDPM to MQ, we have a slightly different observation in comparison to what happened previously with AQ [9]. There is no usual quenching of the ^{3}MQ peak at 370 nm, instead there was an abnormal increase in absorption throughout the wavelength region 340–600 nm as shown in Fig. 2. Nevertheless, peaks corresponding to the radical cations of all the bases, TEA$^{\bullet+}$, DMA$^{\bullet+}$ and DMDPM$^{\bullet+}$ could be still discerned at 380, 460 and 480 nm, respectively [9,14]. In these cases, another peak around 390–400 nm also appeared. There have been reports that MQ$^{\bullet-}$ absorbs around 390 nm [3–6]. So this peak was confirmed to be due to absorption by MQ$^{\bullet-}$. In presence of TEA, an additional hump around 480 nm appears. An investigation of lifetime at both the peaks, 400 and 480 nm, gives nearly equal results, 0.6 μs, which proves that both the peaks are probably due to the formation of similar type of species, MQ$^{\bullet-}$ which also tallies with the literature [6]. Both

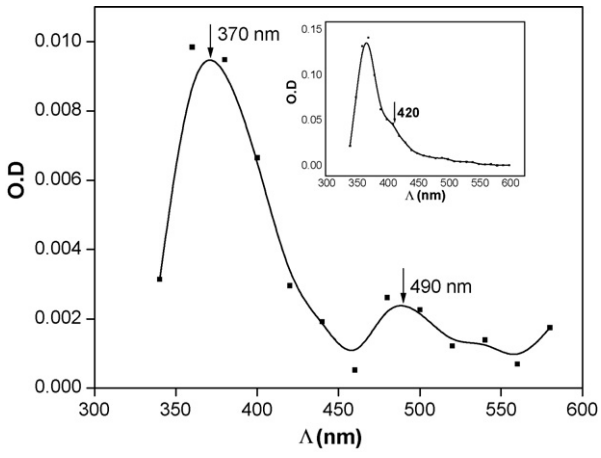


Fig. 1. Transient absorption spectra of MQ (0.2 mM) solution in MeCN at 1.0 μs time delay after laser pulse with excitation wavelength 355 nm. Inset: transient absorption spectra of MQ (0.2 mM) solution in isopropanol after 1.0 μs of laser pulse.

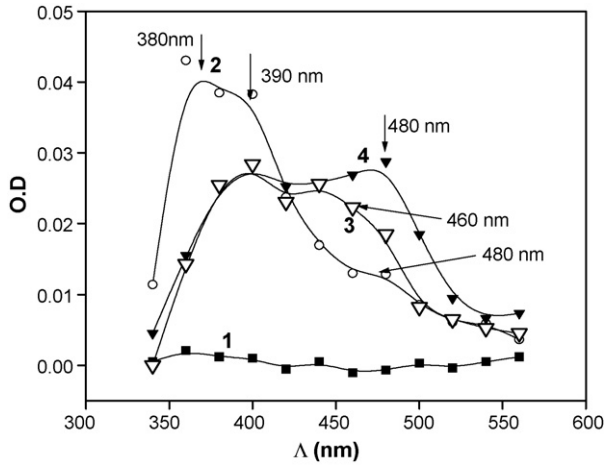


Fig. 2. Transient absorption spectra of (1) MQ (0.2 mM) (■), (2) MQ (0.2 mM)–TEA (0.5 mM) (◯), (3) MQ (0.2 mM)–DMA (0.5 mM) (▽) and (4) MQ (0.2 mM)–DMDPM (0.5 mM) (▼), at a delay of 1.0 μs in MeCN.

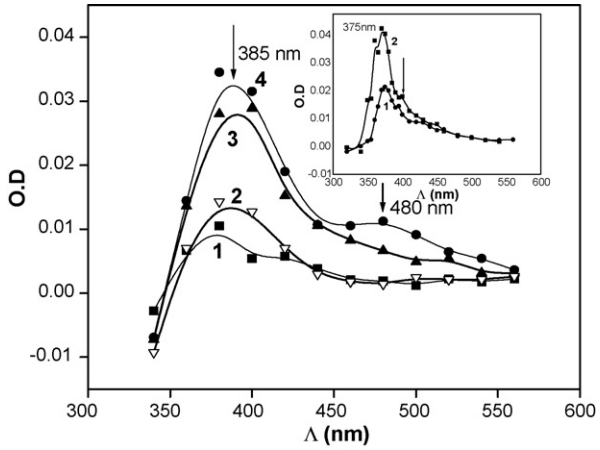


Fig. 3. Transient absorption spectra of (1) MQ (0.2 mM) (■), (2) MQ (0.2 mM)–TEA (0.5 mM) (▽), (3) MQ (0.2 mM)–DMA (0.5 mM) (▲) and (4) MQ (0.2 mM)–DMDPM (0.5 mM) (●), at a delay of 1.0 μs in SDS micelles. Inset: transient absorption spectra of MQ (0.2 mM) in (1) absence (●) and (2) presence of magnetic field (■) after 1.0 μs of laser pulse in SDS micelles.

$DMA^{\bullet+}$ and $DMDPM^{\bullet+}$ absorbs around this 480 nm region, so in their presence the second peak of $MQ^{\bullet-}$, near 480 nm, could not be distinguished clearly. In case of solution containing MQ and TEA, presence of two peaks, the 390–400 nm one due to $MQ^{\bullet-}$ and 380 nm due to $TEA^{\bullet+}$, produces a strong absorption band around 380–400 nm region. Experiments had also been performed using different concentrations of bases. But in each case even low concentration of bases produced results similar to that in Fig. 2. The lifetimes of the RIPs have been calculated using different base concentrations. The values are given in Table 1. The huge increase in absorbance on addition of even very low concentration of bases may be due to the rapid formation of $MQ^{\bullet-}$ with higher absorptivity [6]. Hence an occurrence of ET between MQ and all the three amine bases in MeCN is confirmed.

3.2. Laser flash photolysis: SDS medium

Fig. 3 depicts the transient absorption spectra of MQ (0.2 mM) in absence and presence of all the bases (0.5 mM) in micellar medium. The spectra in presence of DMA and DMDPM are entirely different from those in MeCN medium. However there exists some similarity between the spectra with TEA in both the media. Inset of Fig. 3 depicts the transient absorption spectrum of MQ in SDS. A peak around 375 nm and a hump around 420 nm are observed. Application of an external MF leads to an increase in absorption at these wavelengths. This points towards the formation of radicals at these wavelengths [8,9]. Reports indicate the peaks to be due to $MQH^{\bullet}$ [4,8]. In SDS medium, MQ gets trapped into the hydrophobic part and on laser irradiation, abstracts H atom from the C–H bond of SDS [9,15] resulting in the formation of $MQH^{\bullet}$.

Fig. 4 exhibits peaks on addition of DMA and DMDPM to MQ in SDS. Apparently there is no difference between the two spectra. On addition of DMA and DMDPM both, a peak around 385 nm is observed while on application of field, increase around 375 nm is most prominent. This can be explained by presence of two species which are generated upon addition of bases, firstly MQH^{-} (which is formed on H atom abstraction by $MQ^{\bullet-}$) or MQH_2 (which is formed by abstraction of two H atom by MQ) and secondly $MQH^{\bullet}$. The species MQH^{-} or MQH_2 does not show MFE since geminate characteristics and spin-correlation

Table 1
Lifetimes of different radical ions at different concentrations of bases

Concentration of bases (mM)	Lifetimes of radical ions (μs)			
	$MQ^{\bullet-}$	$DMDPM^{\bullet+}$	$DMA^{\bullet+}$	$TEA^{\bullet+}$
0.05	1.11 (±0.01)	1.14 (±0.04)	1.09 (±0.04)	2.14 (±0.05)
0.1	1.62 (±0.02)	1.43 (±0.02)	1.32 (±0.04)	2.27 (±0.02)
0.5	2.08 (±0.03)	1.76 (±0.03)	1.46 (±0.05)	2.69 (±0.04)

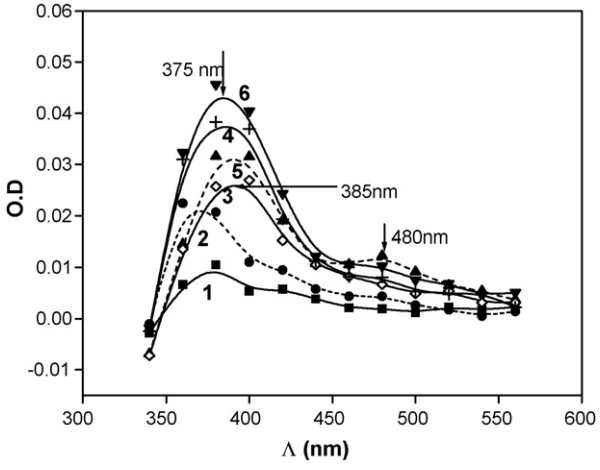


Fig. 4. Transient absorption spectra of MQ (0.2 mM) (1) in absence (■) and (2) presence of magnetic field (●), MQ (0.2 mM)–DMA (0.5 mM) in (3) absence (◊) and (4) presence of magnetic field (+), MQ (0.2 mM)–DMDPM (0.5 mM) in (5) absence (▲) and (6) presence of magnetic field (▼), at a delay of 1.0 μs in SDS micelles.

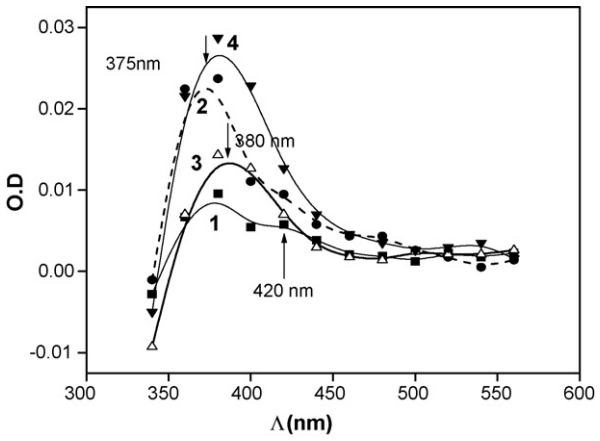


Fig. 5. Transient absorption spectra of MQ (0.2 mM) in (1) absence (■) and (2) presence of magnetic field (●), MQ (0.2 mM) and TEA (0.5 mM) in (3) absence (△) and (4) presence of magnetic field (▼), at a delay of 1.0 μs in SDS micelles.

are lost in the initial RP, whereas $MQH^{\bullet}$ initially formed as a partner of geminate RP ($MQH^{\bullet\bullet}$SDS/DMA/DMDPM) shows distinct MFE [8,9]. MQH^{-} is reported to absorb around 380 nm in aqueous media [4,6]. These results indicate that H atom abstraction becomes the dominant pathway in SDS medium as MQ, DMA and DMDPM gets trapped in the hydrophobic portion and thus $MQH^{\bullet}$ ($\lambda_{max} = 375$ nm) is the predominating species. An increased peak height on addition of bases bears testimony to the fact. The peaks corresponding to the radical cations are not very clear especially in case of DMA. So it is confirmed that ET gets a backseat in comparison to H abstraction in micelles. Still in case of DMDPM a small hump around 480 nm corresponding to $MQ^{\bullet-}$ and $DMDPM^{\bullet+}$ can be discerned (Fig. 3), so the possibility of ET cannot be totally ignored in case of aromatic amines. Actually ET is a distance-dependent phenomenon [16] and so it cannot be ruled out entirely as some DMA, DMDPM molecules will always remain at an appropriate distance from MQ in micelles to induce some ET.

Fig. 5 depicts the field effect on MQ upon addition of TEA. MQ alone exhibits a peak around 375 nm and a hump around 420 nm, which shows a good increase on MF application. Upon addition of TEA, there is a distinct shift in absorption maxima towards 380 nm and a complete absence of 420 nm peak presence of both together being a sure signature of $MQH^{\bullet}$. Now we know $TEA^{\bullet+}$ absorbs around 380 nm so the broad peak can be safely accounted for the presence of both $MQ^{\bullet-}$ and $TEA^{\bullet+}$, and not $MQH^{\bullet}$, hence ruling out every possibility of H abstraction from TEA to MQ in SDS. Still a slight possibility of H atom transfer from C–H bond of SDS to MQ remains in presence of TEA, but a dominant ET and corresponding increased peak heights of RIPs have perhaps eclipsed the 420 nm hump of $MQH^{\bullet}$. TEA being an aliphatic amine is appreciably soluble in water, which restricts it in the aqueous part of micellar media, thus always an appropriate distance from MQ is maintained suitable for ET. Actually H atom transfer requires a prior H bonding between the donor and acceptor [8]. And so this distance totally restricts a possibility of H bonding and hence H atom transfer to MQ. Thus ET remains the only reaction pathway for TEA in MeCN and SDS both.

The reaction scheme for the interpretation of the results in SDS is given below:

$$MQ \rightarrow {}^{1}MQ^{*} \rightarrow {}^{3}MQ^{*} \quad (1)$$

$${}^{3}MQ + RH\,(SDS) \rightarrow {}^{3}(MQH^{\bullet\bullet}R) \quad (2)$$

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

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

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

$${}^{3}MQH^{\bullet} + RH \rightarrow {}^{3}MQH_{2} \quad (6)$$

$${}^{3}MQ^{*} + DMA \rightarrow {}^{3}(MQ^{\bullet-}\,DMA^{\bullet+}) \quad (7)$$

$${}^{3}(MQ^{\bullet-}DMA^{\bullet+}) \underset{MF}{\overset{HFI}{\longleftrightarrow}} {}^{1}(MQ^{\bullet-}DMA^{\bullet+}) \quad (8)$$

$${}^{3}(MQ^{\bullet-}\,DMA^{\bullet+}) \rightarrow {}^{3}MQ^{\bullet-} + {}^{3}DMA^{\bullet+}\ (\text{escape product}) \quad (9)$$

$${}^{3}MQ^{*} + DMDPM \rightarrow {}^{3}(MQ^{\bullet-}\,DMDPM^{\bullet+}) \quad (10)$$

$${}^{3}(MQ^{\bullet-}DMA^{\bullet+}) \underset{MF}{\overset{HFI}{\longleftrightarrow}} {}^{1}(MQ^{\bullet-}DMDPM^{\bullet+}) \quad (11)$$

$${}^{3}(MQ^{\bullet-}\,DMDPM^{\bullet+}) \rightarrow {}^{3}MQ^{\bullet-} + {}^{3}DMDPM^{\bullet+}\ (\text{escape product}) \quad (12)$$

$${}^{3}MQ^{*} + TEA \rightarrow {}^{3}(MQ^{\bullet-}\,TEA^{\bullet+}) \quad (13)$$

$${}^{3}(MQ^{\bullet-}TEA^{\bullet+}) \underset{MF}{\overset{HFI}{\longleftrightarrow}} {}^{1}(MQ^{\bullet-}TEA^{\bullet+}) \quad (14)$$

$${}^{3}(MQ^{\bullet-}\,TEA^{\bullet+}) \rightarrow {}^{3}MQ^{\bullet-} + {}^{3}TEA^{\bullet+}\ (\text{escape product}) \quad (15)$$

Following steps of reactions are for hydrogen abstraction in case of DMA and DMDPM with MQ:

$${}^{3}MQ^{*} + DMA \rightarrow {}^{3}(MQH^{\bullet\bullet}\,DMA)\ (\text{H abstraction}) \quad (16)$$

$${}^{3}(MQH^{\bullet\bullet}DMA) \underset{MF}{\overset{HFI}{\longleftrightarrow}} {}^{1}(MQH^{\bullet\bullet}DMA) \quad (17)$$

$${}^{3}MQ^{*} + DMDPM \rightarrow {}^{3}(MQH^{\bullet\bullet}\,DMDPM)\ (\text{H abstraction}) \quad (18)$$

$${}^{3}(MQH^{\bullet\bullet}DMDPM) \underset{MF}{\overset{HFI}{\longleftrightarrow}} {}^{1}(MQH^{\bullet\bullet}DMDPM) \quad (19)$$

Now a question arises as to why DMA, DMDPM fails to transfer their H to MQ in MeCN? In micelles close proximity of MQ and aromatic amines are established on account of their entrapment in hydrophobic region, which supports H bonding and a consequent H atom transfer from methyl moiety of DMA, DMDPM to MQ [17]. Whereas in organic homogeneous

medium, such closeness is not favored due to random distribution of molecules hence possibility of H bonding is upset and ET is prevalent.

In our previous work, we observed AQ exhibited a dominance of ET with DMA and DMDPM in MeCN and SDS both [9]. The reverse behavior in comparison to MQ is attributed to the failure of H bonding between H of amines with oxygen of quinone in AQ due to the intervening bulky phenyl ring. A small methyl group in MQ does not provide any barrier to H bonding between amines and quinone, while a larger phenyl moiety in AQ can, thus upsetting slightest possibility of H atom transfer from amines to AQ in SDS regardless of their close location. Hence AQ will always prefer a dominant ET while MQ will exhibit a fluctuating behavior depending on structure of donors and medium. Hence we observe a dominance of ET with TEA and H abstraction with DMA, DMDPM in micellar media using MQ.

4. Conclusion

This work illustrates the differential behavior of aromatic and aliphatic amines with MQ in MeCN and SDS micelles. In MeCN, all the donor amines undergo ET with MQ. In contrast, in SDS medium, DMA and DMDPM remain closely sequestered in the hydrophobic region along with MQ on account of their bulky phenyl moiety, thus promoting H abstraction as the dominant pathway of reaction. While small TEA molecules remains confined in the aqueous part, at a suitable longer distance from MQ, supporting only ET as the dominant mechanism. Hence a switchover from ET to H abstraction is possible in hydrophobic micellar medium by a mere introduction of bulky phenyl rings within amine bases. Increase in steric congestion within bases will always thus lead to H abstraction. Again a suitable explanation for the different behavior of AQ with similar bases has been provided. An extra phenyl ring in AQ being responsible for inhibiting H abstraction, always maintaining a dominant ET chemistry with simple amine bases in MeCN and SDS. Thus an introduction of steric crowding on reacting molecules can change their reaction pattern.

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References

[1] B.K. Sinha, C.F. Chignel, Chem. Biol. Interact. 28 (1979) 301.
[2] W.A. Morgan, J. Biochem. Toxicol. 10 (1995) 227.
[3] J.R. Wagner, J.E. van Lier, L.J. Johnston, Photochem. Photobiol. 52 (1990) 333.
[4] T. Melvin, E. Bothe, D. S-Frohlinde, Photochem. Photobiol. 64 (1996) 769.
[5] G.J. Fisher, E.J. Land, Photochem. Photobiol. 37 (1983) 27.
[6] I. Amada, M. Yamaji, S. Tsunado, H. Shizuka, J. Photochem. Photobiol. A: Chem. 95 (1996) 27.
[7] Y. Gao, J. Chen, Y. Pan, X. Zhuang, S. Yu, Colloids Surf. A: Physicochem. Eng. Aspects 287 (2006) 126.
[8] T. Sengupta, S.D. Choudhury, S. Basu, J. Am. Chem. Soc. 126 (2004) 10589.
[9] A. Chowdhury, S. Basu, J. Lumin. 121 (2006) 113.
[10] I.R. Gould, N.J. Turro, M.B. Zimmt, Adv. Phys. Org. Chem. 20 (1984) 1.
[11] U.E. Steiner, T. Ulrich, Chem. Rev. 89 (1989) 51.
[12] K. Bhattacharya, M. Chowdhury, Chem. Rev. 93 (1993) 507.
[13] D.K. Palit, H. Pal, T. Mukherjee, J.P. Mittal, J. Photochem. 37 (1987) 95.
[14] H.N. Ghosh, H. Pal, A.V. Sapre, J.P. Mittal, J. Am. Chem. Soc. 115 (1993) 11722.
[15] Y. Tanimoto, C. Jinda, Y. Fujiwara, M. Itoh, J. Photochem. Photobiol. A: Chem. 47 (1989) 269.
[16] J.R. Bolton, N. Mataga, G. McLendon, Adv. Chem. Series 228, Electron Transfer in Inorganic, Organic and Biological Systems, Am. Chem. Soc., Washington, DC, 1991.
[17] N.J. Turro, R. Engel, J. Am. Chem. Soc. 91 (25) (1969) 7113.