

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.

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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 sam-

ple 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.

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 μ s time delay after laser pulse is shown in Fig. 1. There is a strong absorption maximum at 370 nm with lifetime of 0.8 μ s. 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 μ s, 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 μ s, 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

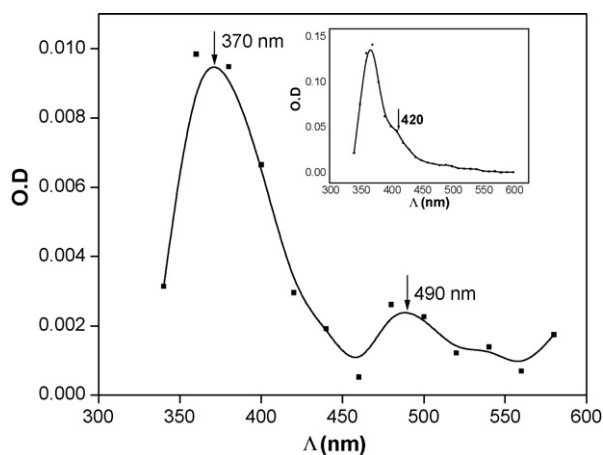
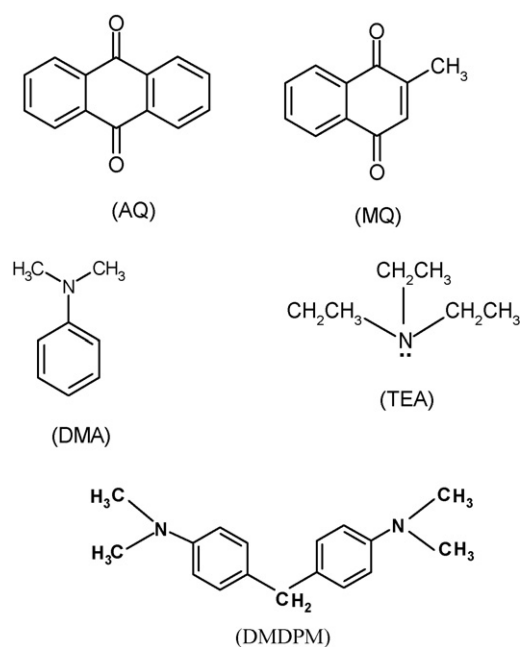


Fig. 1. Transient absorption spectra of MQ (0.2 mM) solution in MeCN at 1.0 μ s time delay after laser pulse with excitation wavelength 355 nm. Inset: transient absorption spectra of MQ (0.2 mM) solution in isopropanol after 1.0 μ s of laser pulse.

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