Excited state dynamics of Michler’s ketone: a laser flash photolysis study

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Abstract—Steady state absorption and fluorescence as well as the time resolved absorption studies in the pico and subpicosecond time domain have been performed to characterize the excited singlet and triplet states of Michler’s ketone (MK). The nature of the lowest excited singlet (S_1) and triplet (T_1) states depends on the polarity of the solvent — in nonpolar solvents they have either pure nπ* character or mixed character of nπ* and ππ* states but in more polar solvents the states have CT character. Concentration dependence of the shapes of the fluorescence as well the excited singlet and triplet absorption spectra provide the evidence for the association of the MK molecules in the ground state.

INTRODUCTION

One of the widely studied and important photochemical reactions undergone by the aromatic carbonyl compounds is the photoreduction by hydrogen atom abstraction from the suitable hydrogen atom donors, may be the solvent or another solute [1–15]. Effects of the substituent groups as well as the solvents towards these photoreduction reactions have been well studied by different groups in order to elucidate the nature of the excited triplet states. The reactivity of this class of compounds has been shown to depend on the electron distribution in the lowest energy excited triplet (T_1) state, i.e. whether it is nπ*, ππ* or charge transfer (CT) state [7, 10, 11, 16]. The relative positions of these three kinds of excited

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states of the aromatic carbonyl compounds, both in the singlet as well as in the triplet manifold, have been seen to depend on the nature of the substituent as well as the solvent [17–20]. A vast number of studies on the reactivity of these compounds have established that the nπ* triplet state is highly reactive towards the photoreduction reaction by hydrogen atom abstraction in comparison with that of the ππ* or CT triplet state [10, 11, 17, 21–23].

Benzophenone, the parent of the aromatic carbonyl compounds, has the lowest energy excited singlet and triplet states of nπ* configuration in all kinds of solvents [24, 25]. The triplet state, which is produced with a quantum yield of unity from its precursor singlet state via intersystem crossing process, is highly reactive towards photoreduction reaction [17, 26]. However, on substitution with electron donating groups, such as OH, OCH₃, NH₂ and N(CH₃)₂ onto the aromatic rings of benzophenone, the relative positions of the nπ*, ππ* and CT states in either of the singlet or the triplet manifolds are largely affected by the solvent polarity [17–19, 26, 27]. Hence, the reactivity of the substituted benzophenone is largely varied in different kinds of solvents.

Michler’s ketone (MK) [4,4’-bis-(dimethylamino)-benzophenone] has been the subject of many investigations for its interesting photophysical and photochemical properties [18, 19, 28–32]. MK exhibits temperature dependent phosphorescence and transient triplet–triplet absorption spectra at low temperature [29]. These results have been interpreted in terms of solvation and conformational changes in the triplet state. The triplet yield for MK is strongly dependent on the solvent characteristics and varies from near unity in hydrocarbon solvents to very small value (<0.2) in alcoholic media [19]. Suppan [31] not only reported a pronounced dependence of the reactivity of the triplet of MK on the nature of the solvents but also on the excitation wavelength. However, systematic work of Schuster et al. [19] on this problem proved that this wavelength dependence of the reactivity of the triplet and the photoreduction yield is rather related to the dependence of the triplet lifetime on MK concentration due to self-quenching reaction and product absorption in the excitation wavelength. Schuster et al. [19] also presented some arguments in relation to the possible formation of triplet excimers. Liptay et al., however, concluded from their steady state fluorescence anisotropy study in ethanol that molecules of MK form molecular aggregates of large mass by association and the excited state of MK has an unusually short lifetime which is shorter than the relaxation time for orientational redistribution of the solvent molecules [32]. In this work, we have performed the laser flash photolysis study in sub-pico and picosecond time domain in different kinds of solvents to investigate the nature of the excited singlet and triplet states of MK, their lifetimes as well as to provide evidence regarding the association of MK molecules in solution from their transient absorption characteristics.