INTRAMOLECULAR PROTON TRANSFER AND ENERGY RELAXATION IN ORTHO-HYDROXYBENZOPHENONE

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Picosecond laser studies of excited state energy relaxation in *o*-hydroxybenzophenone in hexane and ethanol are reported. The effects of intra- and inter-molecular hydrogen bonding on the ultrafast decay channels to the ground and triplet states and the photostability of the molecule are discussed.

Hydrogen, whether as an atom or a proton, plays a key role in the structures, reactions and energy relaxation mechanisms of molecules. This is reflected in the observation that the acid equilibrium constants can differ by many orders of magnitude between the excited and ground states of many molecules [1,2]. Hydrogen bonding characteristics can also vary dramatically between the ground and excited states. New and efficient pathways for energy dissipation, not otherwise available to the excited molecule, are made possible by changes in hydrogen bonding [1–23]. The rapid intramolecular proton transfer, first discovered in fluorescence studies of methylsalicylate [2,3], is the origin of photochemical stability in a number of aromatic and heterocyclic compounds [24,25]. A dramatic example of the effectiveness of these proton dependent relaxation processes is seen in a comparison of the excited state reactivities of benzophenone and ortho-hydroxybenzophenone [21–23]. Benzophenone in its excited triplet state can abstract a hydrogen atom from an alcohol with a quantum yield of one [22] and from hexane with a quantum yield of 0.55 [22]. The long-lived triplet state is the key state in this photoreduction process since the intersystem crossing to the triplet from the excited singlet occurs in about 10 ps [26,27]. In ortho-hydroxybenzophenone (OHBP) no photoreduction is observed in hexane or in alcohol [23]. The marked difference between benzophenone and ortho-hydroxybenzophenone has been attributed to the rapid dissipation of energy in both the excited singlet and triplet states [14,15,19,21,23]. A new radiationless pathway for energy relaxation is provided by the intramolecular hydrogen bond in *o*-hydroxybenzophenone, e.g. the new pathway could result from the shift of the ortho-hydroxy group proton toward the carbonyl oxygen in the excited singlet and triplet states.

In this communication we present some preliminary results from picosecond laser studies on the pathways and rates for these ultrafast energy-dissipating processes which effectively preclude chemical reactions in photoexcited ortho-hydroxybenzophenone.

The experimental system was based on a mode-locked Nd^{+3} : YAG laser. Solutions containing OHBP (3.3×10^{-3} M) were excited by a single pulse at the third harmonic, 354.7 nm. At this wavelength, the pulses possessed fwhm values of ⩽25 ps. Transient absorption results were obtained by probing the sample with a pulse at 354.7 nm, 532 nm, or a wavelength generated by stimulated Raman scattering in a liquid. The time separation between excitation and probe pulse was controlled by a variable optical delay line.

In a non-hydrogen bonding solvent such as hexane the intramolecular hydrogen bond provides an efficient channel for radiationless decay from the excited singlet state back to the ground state. This rapid relaxation is manifested by the ground state repopulation kinetics determined by probing at 354.7 nm (fig. 1a). The

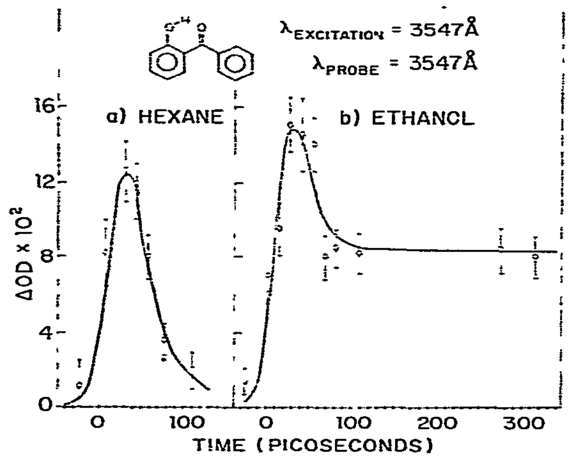

Fig. 1. Ground state repopulation dynamics of OHBP in (a) hexane and (b) ethanol at room temperature. Solid lines are the theoretical curves.

theoretical curve [‡] shown in fig. 1a corresponds to an e^{-1} ground state repopulation time of 35 ± 5 ps. This measurement of ground state repopulation does not however establish whether the triplet state participates in the decay process [21]. To determine if intersystem crossing to the triplet is important, picosecond absorption measurements were carried out at 532 nm. It is in this broad region that triplet benzophenone absorbs strongly and, as we shall discuss shortly, triplet OHBP in the solvent ethanol absorbs as well. In hexane, however, no absorption was observed at any time delay between the excitation and probe pulses. We therefore conclude that intersystem crossing is not important and the lack of reactivity in hexane is due to the ultrafast relaxation from S_1 back to the ground state, perhaps involving a structurally different intermediate state.

In ethanol, on the other hand, the experimental results indicate that the *intermolecular* hydrogen bonding between OHBP and the ethanol molecules modifies the *intramolecular* hydrogen bonding and thereby alters the pathways for energy relaxation [23]. The ground state repopulation measurement (fig. 1b) shows that some fraction of the excited molecules return to the ground state in approximately 30 ps, and that the remaining fraction is in a long-lived excited state. The probe absorption at 532 nm (fig. 2) yields a risetime of less than 15 ps and indicates the presence of a relatively long-lived excited state having a lifetime of 1.5 ns. To demonstrate that this long-lived state is the triplet state of OHBP, we carried out an intermolecular triplet–triplet energy transfer experiment with 1-methylnaphthalene as the acceptor. If the triplet of OHBP was being generated, then at a high concentration of 1-methylnaphthalene the triplet of OHBP should transfer its energy to 1-methylnaphthalene and the triplet of 1-methylnaphthalene should be produced. This is precisely what we observed, namely quenching of the absorption at 532 nm and the appearance of an absorption at 406 nm, the region of known absorption by 1-methylnaphthalene in its lowest triplet state. The 1.5 ns lifetime of the triplet state molecule (fig. 2), consistent with an estimate of less than 10 ns based on quenching experiments in ethanol [23], is shorter by a factor of 10^6 than triplet benzophenone in inert solvents, i.e. solvents which do not react with triplet benzophenone.

It should be noted that unlike studies [28,29] on the ortho-alkyl phenyl ketones we find no evidence for only one triplet in an alcohol solvent. In the ortho-alkyl phenyl ketones two triplets having very different lifetimes have been observed and shown to arise from the syn- and anti-conformers of the molecule. In ortho-hydroxybenzophenone we find no evidence for two types of triplets arising from the two conformers.

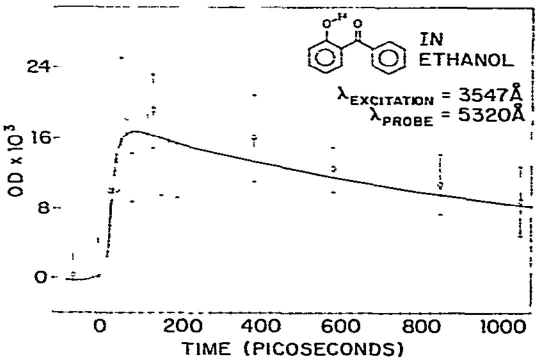

Fig. 2. Triplet state transient absorption of OHBP in ethanol at room temperature. Solid line is the theoretical curve.

[‡] The theoretical curves (solid lines in figs. 1 and 2) were obtained by varying the rate constants for the rise and decay of the transient absorption to obtain best fit with experiments using 25 ps fwhm excitation and probe pulses.

Since the risetime of the OHBP triplet in ethanol is significantly less than the ground state repopulation time we conclude that the triplet and ground states are not being generated from a common precursor state. One view consistent with these results would be the presence of two distinct ground state species in ethanol which differ only in their hydrogen bonding interactions with the solvent. One could be an intramolecularly hydrogen bonded species which on excitation to its excited singlet state rapidly decays to the ground state or to some intermediate structure via the radiationless channel provided by the intramolecular hydrogen bond. For these molecules no triplets are produced. The other ground state population could (at the time of excitation) be those molecules which have intermolecular hydrogen bonds to the solvent but do not have intramolecular hydrogen bonds. These intermolecularly hydrogen bonded molecules on excitation to their singlet states cross over to their triplet states with high efficiency as in the case of unsubstituted benzophenone. The 1.5 ns lifetime observed for the triplet could be interpreted as a measure of the interconversion time to an intramolecularly hydrogen bonded species which can then decay efficiently to a ground state structure utilizing the intramolecular hydrogen bond as a dissipative pathway.

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