Pergamon

Tetrahedron Letters 40 (1999) 3995–3998

TETRAHEDRON
LETTERS

Photochemical formation of 4'-N,N-dimethylamino-3-hydroxyflavone in hydrocarbon solutions of 4-N,N-dimethylamino-2'-hydroxychalcone.

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Received 8 January 1999; accepted 24 March 1999

keywords: Chalcones; Flavones/flavanones; Photochemistry; Fluorescence

Abstract: The appearance of a fluorescence emission band at 553 nm from hydrocarbon solutions of 4-N,N-dimethylamino-2'-hydroxychalcone was found to be sensitive to the presence of dissolved oxygen and exposure to ambient visible light. The 390 nm peak of this band's excitation profile along with the fluorescence maximum suggest that a low yield photoreaction occurs leading to the formation of the highly fluorescent 4'-N,N-dimethylamino-3-hydroxyflavone. © 1999 Elsevier Science Ltd. All rights reserved.

Substituted chalcones are of particular interest because of their role as precursors in the biological formation of flavonoids[1], their potential nonlinear optical properties[2], and as fluorescent probes for micellar solutions[3]. The presence of several functionalities provides intriguing opportunities to investigate the electronic properties of conjugated systems. The possibility of producing charge transfer effects by placing electron-donating groups on the styrenyl moiety has been investigated[4]. Studies of excited state proton transfer in flavonols[5] and 2'-hydroxychalcone[6,7] have recently been reported. During our investigations of solvent effects on emission from compounds capable of exhibiting charge transfer behavior, an anomalous luminescence spectrum was observed from cyclohexane solutions of 4-N,N-dimethyamino-2'-hydroxychalcone (dmahc). While a linear correlation is obtained for a Lippert-Mataga plot of Stokes shifts versus solvent polarity for solutions of dmahc in benzene, methylene chloride, dioxane, diethyl ether, chloroform, ethyl acetate, acetone and acetonitrile, the data from the cyclohexane solutions deviates significantly from the linear plot. We have assigned this fluorescence to 4-N,N-dimethylamino-3-hydroxyflavone (dmahf) produced in a low yield photoreaction caused by the presence of oxygen and the ambient light.

Experimental. 4'-N,N-Dimethylamino-2'-hydroxychalcone was synthesized by base-catalyzed aldol condensation of 2'-hydroxyacetophenone and 4-N,N-dimethylaminobenzaldehyde, as described elsewhere[8]. Luminescence grade cyclohexane (Fluka) and HPLC grade n-pentane (Fisher) were used to prepare solutions for emission spectroscopy. Fluorescence data were recorded with a Perkin-Elmer LS-5 fluorimeter.

Results. The fluorescence spectrum obtained from 406 nm excitation of an air saturated 1 x 10^{-5} M dmahc cyclohexane solution is shown in Figure 1. A band at 553 nm and a less intense band at 461 nm are observed in this trace. The excitation profile of the more intense 553 nm band displays a maximum at 390 nm, which does not correspond to the 406-434 nm band seen in the absorption spectrum of this solution.

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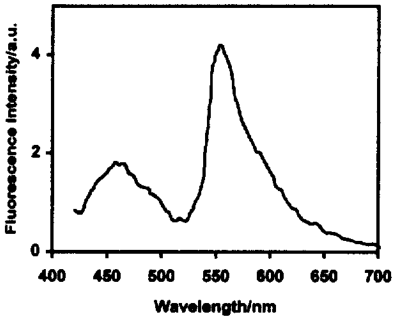


Figure 1. Dispersed fluorescence spectrum obtained from 370 nm excitation of 1 x 10^{-5} M dmahc in cyclohexane, note maxima at 461 nm and 553 nm.

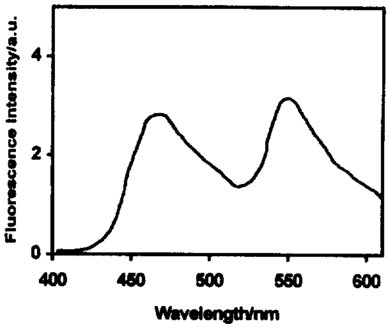


Figure 2. Dispersed fluorescence from 5 x 10^{-4} M dmahc in cyclohexane. The sample was purged with N_2 and kept in the dark prior to excitation.

Unfortunately, the excitation profile of the lower intensity 461 nm band could not be accurately measured due to interference of solvent Raman lines at low concentrations, and of the typical distortion of excitation spectra at higher concentrations.

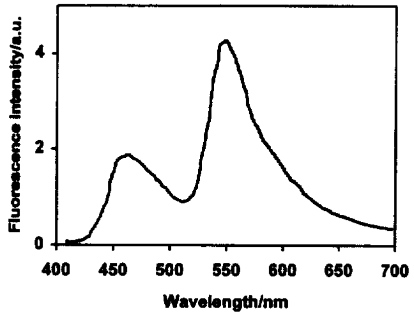


Figure 3. Dispersed fluorescence from 5 x 10^{-4} M dmahc in cyclohexane. The sample was reoxygenated and exposed to 25 minutes of 337 nm laser radiation.

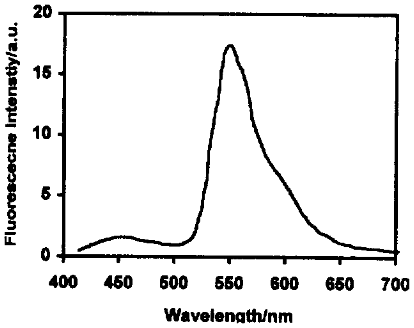


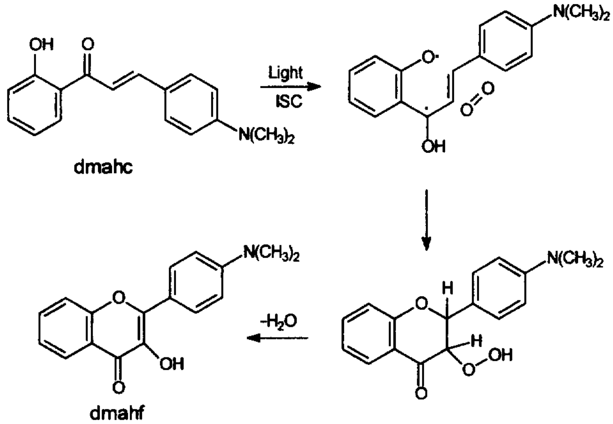
Figure 4. Dispersed emission form 5 x 10^{-4} M dmahc cyclohexane solution after 45 minutes of exposure to 337 nm laser radiation.

Emission spectra were obtained from solutions prepared identically, but under conditions of subdued light and stored in the dark. The data presented in Figure 2 represent the corresponding emission data recorded promptly after dry nitrogen gas was bubbled through the solution in order to remove dissolved oxygen. These spectra were recorded so as to minimize exposure to both ambient light and the monochromatic excitation source. Under these conditions the two bands are seen to be of comparable intensities (Figure 2). The intensity of the 461 nm band in this spectrum has remained unchanged; it is the intensity of the 553 nm band that is reduced. Exposure of this sample to 337 nm and 400 nm laser excitation for 25 minutes results in a solution which yields fluorescence spectra (illustrated in Figure 3) with relative intensities similar to those observed in samples exposed to ambient light as seen in Figure 1. Further illumination results in an overwhelming increase in the relative intensity of the 553 nm band with no noticeable diminishment of the 461 nm band. The dispersed emission spectrum for the reoxygenated sample exposed to laser radiation for a total of 45 minutes is presented in Figure 4. Similar results were observed for n-pentane solutions of dmahc (data not shown).

Discussion. The increase in the intensity of the 553 nm emission band relative to the 461 nm band on exposure of the sample to light indicates that the former band is due to a photo-product not present in fresh solution kept in the dark. This hypothesis is supported by the failure of the excitation spectrum of this emission to reproduce the dmahc absorption spectrum. The 553 nm emission band corresponds to the emission spectrum observed for methylpentane solutions of 4'-N,N-dimethylamino-3-hydroxyflavone, dmahf[9]. Similar data are also reported for benzene solutions of this compound[5], where this emission has been determined to originate from the tautomeric form of dmahf following excited state proton transfer in non-polar solvents. The excited state transfer of the hydroxy proton to the carbonyl oxygen in the flavone forms the tautomer that is the dominant form in non-polar solvents. The excitation spectrum we obtained for the 553 nm band (data not shown) matches the absorption spectrum of dmahf reported in the literature[9]. The quantum yield of fluorescence (Φ_f) for dmahf is estimated to be 0.15, based on the reported lifetimes of dmahf[8], and $\Phi_f \approx 0.36$ for 3-hydroxy-flavone[10]. This value of Φ_f is much greater than the value of $\Phi_f = 0.003$ found for dmahc[11]. This is consistent with the failure to observe any change in the absorption spectrum of the photolyzed sample. The fifty fold difference in Φ_f accounts for the increasing fluorescence intensity observed following illumination of the dmahc sample, shown in Figures 3 and 4, and suggests that even a very low quantum yield photoreaction for the formation of the dmahf from dmahc would conform to the observations reported here.

A similar photoreaction has been reported by Chou et al. for the formation of 3-hydroxyflavone from 2'-hydroxychalcone[6]. The mechanism proposed by these authors involves excited state nucleophilic attack by the phenolic oxygen on the β-carbon of triplet 2'-hydroxychalcone which, in the presence of $^3O_2$, gives 2-peroxyflavanone. Chou et al. exclude the possibility of a $^1O_2$ mechanism for the 2'-hydroxychalcone photoreaction based on the lack of increase in quantum yield for 3-hydroxyflavone formation in C_6D_{12} solutions relative to C_6H_{12} solutions, where the $^1O_2$ lifetime is ~ 15 times lower[9]. As pointed out in their paper, in order for intramolecular cyclization to occur the molecule must adopt the energetically less favorable *s-trans* conformation. Nonetheless, these authors argue that the transoid conformation achieves some stability from interactions between the phenolic oxygen and the electron-deficient β-carbon. In CCl_4 solutions 20-25% of 2'-hydroxychalcone is found in the *s-trans* conformation as determined by IR spectrometry and analysis of NMR spectra[12]. Calculations based on semi-empirical AM1 methodology adapted to explain the measured dipole moment of 2'-hydroxychalcone suggest that as much as 56.1% of the *s-trans* conformer is present at equilibrium[12]. These facts tend to support this mechanism insofar as to provide a reasonable population of *s-trans* conformers capable of undergoing the necessary additional conformational change needed to place the 2'-hydroxy group in proximity to the beta-carbon of the α,β-unsaturated ketone.

Cyclization also necessitates breaking the intramolecular hydrogen bond between the phenolic and carbonyl oxygens. In nonpolar solvents spectroscopic studies indicate that intramolecular hydrogen bonding interactions in dmahc are substantial[13]. In light of this, we propose a slightly different mechanism for the reaction, as illustrated in Scheme 1. Excited state hydrogen transfer facilitates rotation about the carbonylphenol ring C-C bond. The biradical species generated by hydrogen abstraction cyclizes in the presence of $^{3}O_2$ to produce the peroxyflavanone. Subsequent loss of water, possibly via an α–diketone intermediate, generates the enol photo-product, 4'-N,N-dimethylamino-3-hydroxyflavone (Scheme 1). The possibility that this photoreaction is promoted by excited state intramolecular hydrogen transfer from the triplet state of dmahc warrants further investigation.



Scheme 1

Acknowledgment. Funds to support this work were provided by PRAP and Faculty Research and Development grants administered through Hofstra University.

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