

ARTICLES

Effect of Pressure on the Excited-State Proton Transfer of 3-Hydroxyflavone[†]

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We have investigated the effect of pressure on excited-state intramolecular proton transfer (ESIPT) in 3-hydroxyflavone dissolved in four polymeric matrixes—poly(methyl methacrylate) (PMMA), poly(vinyl acetate) (PVAc), poly(acrylic acid) (PAA), and cellulose acetate (CAC). We have also determined the change in normalized equilibrium constant (K^*) and the change in partial molar volume ($\Delta\bar{V}$) as a function of pressure. In all matrixes, with an increase of pressure, the fluorescence intensity of the phototautomer decreases. In PMMA, PVAc, and CAC, the equilibrium constant (K) and change of partial molar volume ($\Delta\bar{V}$) are sensitive to pressure below 30 kbar. The results imply that ESIPT of 3-hydroxyflavone is effectively suppressed by pressure. The anomalous proton-transfer behavior of 3-hydroxyflavone in PAA can be explained by protonation of the carbonyl oxygen.

Introduction

Excited-state intramolecular proton transfer (ESIPT) has received considerable attention throughout the last two decades.¹ One of the most striking examples is 3-hydroxyflavone. The anomalous photophysical properties of 3-hydroxyflavone were first reported in detail by Sengupta and Kasha.² The fluorescence spectrum of 3-hydroxyflavone has one or two bands whose intensity is sensitive to temperature and the solvent properties. It was proposed that the two fluorescence bands correspond to fluorescence from the Franck–Condon excited state and the phototautomer produced by ESIPT. Since then, the photophysics of 3-hydroxyflavone has been extensively studied in various solvents via steady-state and time-resolved spectroscopy.^{3–9} Although there is some disagreement as to whether the fluorescence decay of the normal form N^* is single^{3,4} or double⁵ exponential, in all cases the proton transfer from the 3-hydroxy to the carbonyl oxygen was found to be rapid (in the scale of 10 ps).⁴ The lifetime of the excited-state tautomer T^* varied considerably with solvent from a few hundred picoseconds to several nanoseconds.

To date, most studies of ESIPT in 3-hydroxyflavone focused on the effects of hydrogen-bonding solvents, impurities in nonpolar solvents, or temperature. Few papers report the effect of high pressure on ESIPT.¹⁰ In this paper, we report on the effect of high pressure on ESIPT in 3-hydroxyflavone in solid solution.

Experimental Section

3-Hydroxyflavone (99%) and methoxyflavone (99%) were obtained from Aldrich and recrystallized in methanol before use.

[†] This work was supported in part by the U. S. Department of Energy, Division of Materials Science Grant DEFG02-91ER45439 through the University of Illinois at Urbana-Champaign, Frederick Seitz Materials Research Laboratory.

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Poly(methyl methacrylate) (PMMA, medium molecular weight), poly(vinyl acetate) (PVAc, medium molecular weight, $T_g \approx 35^\circ\text{C}$), poly(acrylic acid) (PAA, MW=250,000, $T_g = 106^\circ\text{C}$), and cellulose acetate (CAC, acetyl content 39.8%) were also obtained from Aldrich. They were used without further purification, because they did not fluoresce when irradiated at the excitation wavelength.

The samples were prepared by dissolving 3-hydroxyflavone (or methoxyflavone) and PMMA, PVAc, or CAC in photometric grade chloroform (PAA was dissolved in photometric grade methanol) and then pouring the transparent solution into a glass dish. After the solvent evaporated at room temperature, the film was dried for several days in a vacuum oven. The concentration of 3-hydroxyflavone and methoxyflavone was 0.05 wt % in all cases. The operation of the high-pressure cell (DAC) has been described in detail elsewhere.^{11–13}

Emission was excited with the 325-nm line of a HeCd laser. The absorption apparatus utilized a xenon lamp, which was transmitted to and from the surface of the diamonds by optical fibers. All emission and absorption spectra were corrected for grating and PMT sensitivity at different wavelengths.

In all cases, the results represented the average of at least two loads. The scatter among the results from different loads was never over $\pm 10\%$. Upon release of pressure, the spectra were highly reversible.

Results and Discussion

1. Pressure Effects on Absorption and Fluorescence Spectra. The absorption and fluorescence spectra of 3-hydroxyflavone in PMMA, PVAc, and CAC have similar shapes and pressure dependence. Typical absorption and fluorescence spectra of 3-hydroxyflavone in CAC and PAA at different pressures are shown in Figures 1 and 2.

3-Methoxyflavone exhibits only one fluorescence band at any pressure. With increasing pressure, the fluorescence intensity

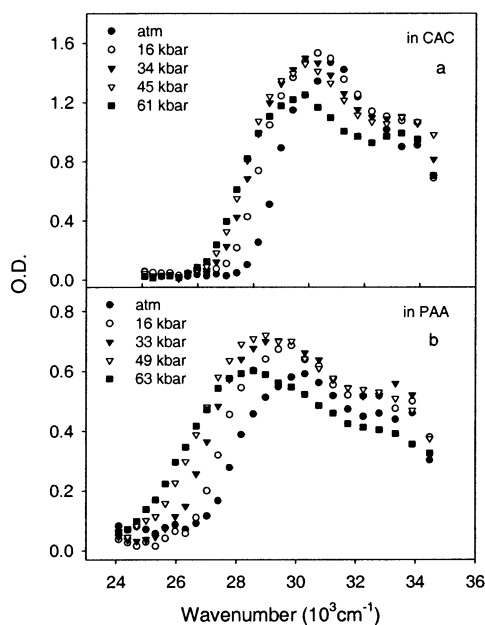


Figure 1. Absorption spectra of 3-hydroxyflavone in CAC (a) and PAA (b).

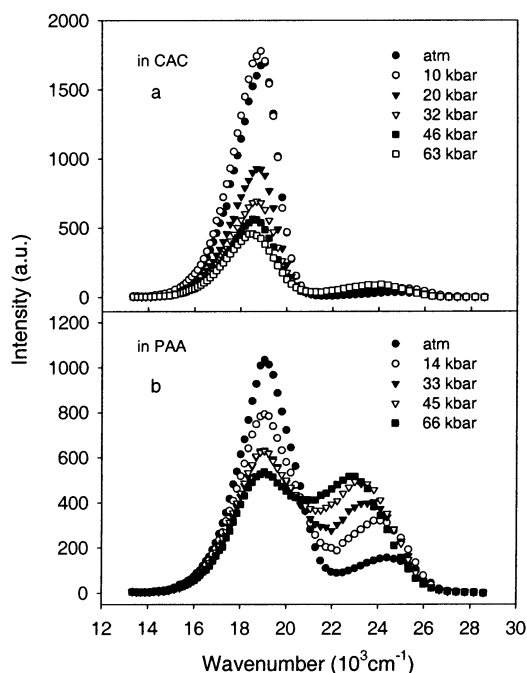


Figure 2. Fluorescence spectra of 3-hydroxyflavone in CAC (a) and PAA (b).

increases and the peak shifts to the red. The fluorescence intensity in CAC (or in PMMA and PVAc) is much lower than that in PAA at the same pressure. Similar behavior was also observed in other flavone compounds in aqueous media at ambient pressure.^{14,15}

Unlike 3-methoxyflavone, 3-hydroxyflavone exhibits two fluorescence bands in PAA and CAC from 1 atm to 65 kbar (see Figure 2), but the high-energy bands are lower in CAC than in PAA. In contrast, PMMA and PVAc only emit in one band at 1 atm, but a new high-energy peak appears gradually above 10 kbar. For 3-hydroxyflavone in CAC, PMMA, and PVAc, the high-energy band corresponds to the fluorescence band of 3-methoxyflavone, so we believe it is the normal state (N*) fluorescence (from the Franck–Condon excited state). The

low-energy band is from the phototautomer (T*) produced by ESIPT. With increasing pressure, the N* peaks increase, and the tautomer peaks decrease in all polymers. There exists the pressure equivalent of an isoemissive point.

In terms of the different absorption spectra and the unique strong normal fluorescence in PAA, the photophysical properties of 3-hydroxyflavone are much more complicated than those in other polymers. The different polarity cannot account for the results. PAA is a weakly acidic polymer. So we only can find the explanation from the acid–base behavior. Wolfbies *et al.*¹⁵ and Rastogi *et al.*¹⁴ have studied the pH-dependent fluorescence of 7-hydroxyflavone and 3-hydroxyflavone, respectively, in acidic alcohol. They both concluded that in moderately acidic solution, the emission is from the phototautomer not from the excited state of the cation (C*), but in more concentrated acid (such as concentrated sulfuric acid), the strongly fluorescent cation becomes the only species in emission.

Based on the above references and our experimental results, we propose Scheme 1 to depict the reactions in PAA. Figure 1b indicates that there exist the neutral and cation molecules in the ground state, although we do not know the exact ratio of these two species. Both neutral and protonated molecules may be excited by a 325-nm laser line to give the fluorescence (tautomer fluorescence). However, the neutral and cation molecules pass a different route to reach tautomers: C* releases a 3-hydroxy proton to solvent (intermolecular proton), while N* proceeds via an intramolecular proton transfer.

2. Effect of Pressure on Equilibrium Constant *K*. The proton-transfer process can be described by the Birks scheme (Scheme 2).

From Scheme 2, the ratio of fluorescence quantum yields is given by

$$\frac{\Phi_T}{\Phi_N} = \frac{k_T' k_{PT}}{k_N' (k_T + k_{-PT})} \quad (1)$$

Because fluorescence quantum yields in eq 1 are measured with respect to the same absorbance and in the same matrices. This ratio (Φ_T/Φ_N) equals the ratio of corresponding integral areas under the two fluorescence bands (A_T/A_N).

Because intramolecular proton transfer occurs on the scale of picoseconds and the tautomer excited state decays on the scale of a couple of nanoseconds, it is reasonable to make an approximation, $k_{-PT} \gg k_T$ at equilibrium. Then the equilibrium constant *K* is approximately:

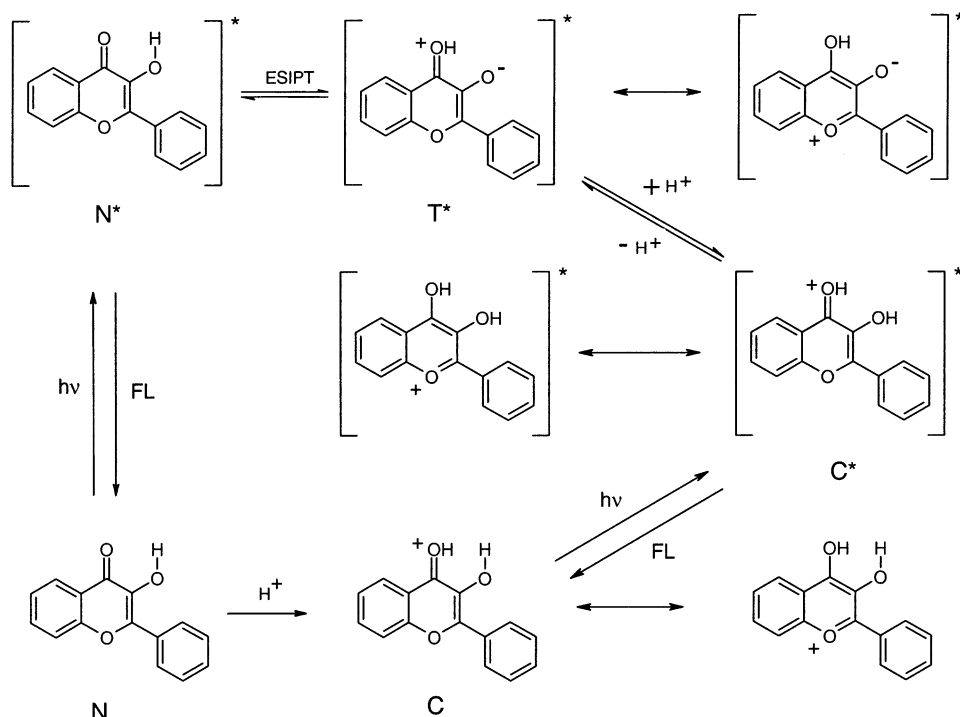
$$K = \frac{k_{PT}}{k_{-PT}} = \frac{A_T k_N'}{A_N k_T'} \quad (2)$$

The normalized equilibrium constant ($K^*(p)$) at pressure *p* is given by

$$K^*(p) = \frac{K(p)}{K(0)} = \frac{A_T(p) k_N'(p) A_N(0) k_T'(0)}{A_N(p) k_T'(p) A_T(0) k_N'(0)} \quad (3)$$

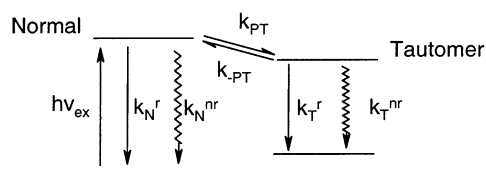
In general aromatic molecules in a solid polymer show negligible pressure dependence of the singlet radiative rate.¹⁶ Assuming k_N' , k_T' are constant, eq 3 becomes

$$K^*(p) = \frac{K(p)}{K(0)} = \frac{A_T(p) A_N(0)}{A_N(p) A_T(0)} \quad (4)$$

SCHEME 1: Ground-State and Excited-State Reactions in PAA^a

^a N, neutral molecule; C, cation; T, tautomer; FL, fluorescence.

SCHEME 2: Kinetic Scheme for the Proton-Transfer Process



The point must be made that both protonated and neutral molecules may exist in PAA, and both kinds of molecules can be excited by a 325-nm laser line. The proton-transfer process in PAA is much more complicated than one can explain by Scheme 2. So eq 4 is not applicable to the proton transfer of 3-hydroxyflavone in PAA. We only present the values of $K^*(p)$ in CAC, PMMA, and PVAc (Figure 3) as a function of pressure. As mentioned above, in PMMA and PVAc, and at pressures less than 10 kbar, only the tautomer bands are observed, so we normalize to $K(10)$ in Figure 3.

$K^*(p)$ decreases rapidly at pressures below 30 kbar and then levels off at about 1/10 to 1/5 of the initial value. Note that the normalized $K^*(p)$ is independent of the matrix. The curves in CAC, PMMA, and PVAc are close, even though the pressure effect on $K^*(p)$ is considerable.

3. Pressure Dependence of $\Delta\bar{V}$. $\Delta\bar{V}$ is the difference in partial molar volume between normal and tautomer states. From eq 3 and elementary thermodynamics, we have

$$\frac{\partial \ln K}{\partial p} = -\frac{\Delta\bar{V}}{RT} \quad (5)$$

Then

$$\Delta\bar{V} = -RT \frac{\partial \ln K}{\partial p} = -RT \frac{\partial \ln (A_T/A_N)}{\partial p} \quad (6)$$

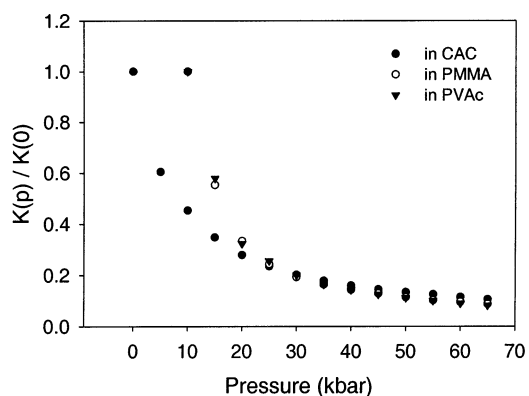


Figure 3. $K^*(p)$ vs Pressure.

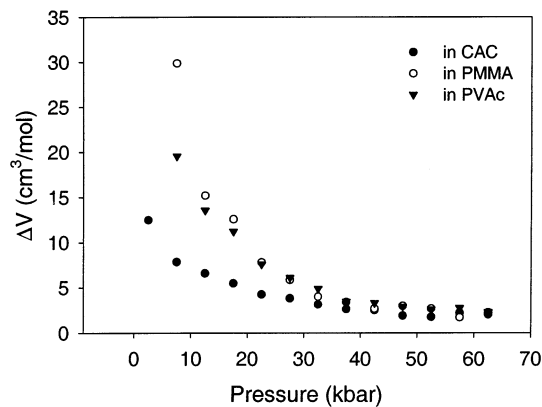


Figure 4. Effect of pressure on $\Delta\bar{V}$.

R is the gas constant ($R = 8.314 \times 10^{-2} \text{ cm}^3 \text{ kbar mol}^{-1} \text{ K}^{-1}$); T is temperature (K). We then calculate $\Delta\bar{V}$ from 2.5 kbar in CAC and from 7.5 kbar in PMMA and PVAc. $\Delta\bar{V}$ in PMMA, PVAc, and CAC turns out to be very sensitive to pressure (Figure 4).

Summary

We have presented the effects of pressure on the excited-state intramolecular proton transfer of 3-hydroxyflavone in four solid matrixes. The conclusion of this work is summarized as follows:

1. Pressure greatly suppresses the formation of phototautomer, resulting in the increase of normal state fluorescence.

2. The abnormal photophysical behavior of 3-hydroxyflavone in PAA is rationalized by the protonation of the carbonyl oxygen.

3. The normalized equilibrium constant $K^*(p)$ and the difference in partial molar volume between normal and tautomer states $\Delta\bar{V}$ decrease rapidly at lower pressures (1 atm–30 kbar). $K^*(p)$ is independent of matrix.

Acknowledgment. We thank the US Department of Energy, Division of Materials Science, for continuing support under Grant DEFG 02-91ER45439 through the Frederick Seitz Materials Research Laboratory at the University of Illinois at Urbana—Champaign.

Supporting Information Available: Effects of pressure on fluorescence spectra of 3-methoxyflavone in CAC (a) and PAA (b) and on the ratio of areas, $A_{\text{HEP}}/(A_{\text{HEP}} + A_{\text{LEP}})$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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