Fluorescence Studies of Excited State Intramolecular Proton Transfer (ESIPT) in Molecules Isolated in Solid Argon: 3-Hydroxyflavone and 2,5-Bis(2-benzoxazolyl)hydroquinone

Bernhard Dick

Max-Planck-Institut für biophysikalische Chemie, Abt. Laserphysik, Am Faßberg, D-3400 Göttingen, Federal Republic of Germany

Fluorescence / Matrix Isolation / Photochemistry / Proton Transfer / Spectroscopy, Ultraviolet / Spectroscopy, Visible

The fluorescence properties of 3-hydroxyflavone and 2,5-bis(2-benzoxazolyl)hydroquinone have been investigated in solid argon matrices at 15 K. In both cases dominant emission from the tautomeric form of the molecules is observed. The excitation spectra of this fluorescence and a weak fluorescence at shorter wavelength show that the latter is due to molecules with a different ground state, presumably dimers or conformers lacking an internal hydrogen bond. For both molecules no fluorescence from the normal form is found indicating the absence of a barrier to excited state intramolecular proton transfer (ESIPT).

1. Introduction

Many molecules with an intramolecular hydrogen bond possess two tautomeric forms, one of which is stable in the ground state, whereas the other is more stable in the first excited singlet state. When the interconversion of both forms merely involves movement of a proton along the hydrogen bond, proton transfer can be a very rapid process. Fig. 1 gives a general level diagram indicating also the structural formulas of the normal and tautomer forms of the molecules 3-hydroxyflavone and 2,5-bis(2-benzoxazolyl)hydroquinone discussed in this article. After electronic excitation of the normal form (A_0) to the first excited state (A_1) the excited state (B_1) of the tautomer is rapidly formed. Fluorescence $B_1 \rightarrow B_0$ from the tautomer displays a large Stokes shift relative to the absorption $A_0 \rightarrow A_1$ of the normal form. This fact lead to the first observation of this effect, later called excited state intramolecular proton transfer (ESIPT), by Weller in 1956 [1]. Since then this process has been investigated numerous times [2, 3]. A question of particular interest is, whether a barrier to proton transfer exists either in the excited state or in the ground state.

A barrier to ESIPT would result in increasing fluorescence from the normal form ($A_1 \rightarrow A_0$) with decreasing temperature. However, with a single exception, in all cases where fluorescence from the normal form was reported [see e.g. 4, 5], it was later found that this emission was due to other conformers [6–9] or complexes with hydrogen bonding impurities [10]. An example thoroughly discussed in the recent literature is 3-hydroxyflavone [5, 10–17]. Complexes are easily formed with traces of impurities when solutions

Ber. Bunsenges. Phys. Chem. *91*, 1205–1209 (1987) –
0005–9021/87/1111–1205 $ 02.50/0

are cooled to form glasses [10]. Such samples display slowly rising tautomer fluorescence wrongly attributed to a barrier in the excited state [12–15]. The preparation of pure samples in organic glasses requires sophisticated techniques and is not always successful [10]. In the search of an alternative preparation technique which yields low-temperature samples of unperturbed molecules we considered matrix isolation. In this article we describe isolation in solid argon as a simple method to avoid the problems encountered with organic glasses. Especially formation of complexes with hydrogen bonding impurities was efficiently suppressed. In addition, excitation spectra in argon matrices are higher resolved than in organic glasses and allow the distinction of different conformers.

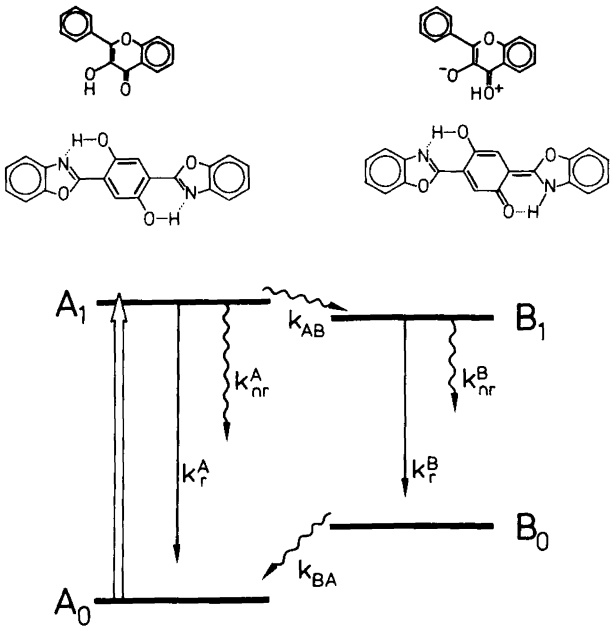

Fig. 1
Schematic energy level diagram for ESIPT. The tautomer (B) is formed from the excited state of the normal molecule (A) with rate constant k_{AB}. The backreaction occurs in the ground state with rate constant k_{BA}. Both molecular forms decays through radiative (k_r) and nonradiative (k_{nr}) processes

The exception mentioned above showing true dual fluorescence is 2,5-bis(2-benzoxazolyl)hydroquinone [18]. ESIPT is a reversible process in this molecule in unpolar solvents, and the equilibrium between both forms is established within few picoseconds [18–20]. Excitation spectra of the isolated cold molecules in a supersonic jet indicate the existence of a small barrier to ESIPT [21, 22]. In liquid solution and organic glasses the situation is not so clear since the relative yield of fluorescence from the normal form seems to decrease with decreasing temperature [23]. In polar solvents the yield of tautomer fluorescence increases indicating a stabilization of the tautomer due to its higher polarity [19]. Conversely, an environment of argon atoms should destabilize the tautomer and make the appearance of a barrier more likely.

In this article we discuss the spectra of 3-hydroxyflavone and 2,5-bis(2-benzoxazolyl)hydroquinone isolated in solid argon. The first molecule was chosen for its sensitivity against complex formation, whereas the latter is the most likely candidate for the observation of a barrier to ESIPT.

2. Experimental

3-Hydroxyflavone was purchased from Eastman and purified by recrystallization from methanol (3 ×) followed by vacuum sublimation (MP 171.5°C). The synthesis and purification of 2,5-bis(2-benzoxazolyl)hydroquinone and its dimethoxyderivative is described in Refs. [18, 24]. These substances were additionally purified by vacuum sublimation.

Argon matrices were deposited by the continuous flow technique with a speed of 1–3 mmol/h onto a sapphire window kept at 15 K by a closed cycle refrigerator cryostat (Leybold ROK 10–300). The sample was dispersed over glass wool and placed into the argon flow. Deposition was controlled through heating of the sample.

The light of a 75 W xenon arc lamp dispersed through a monochromator (Spex 1780, f = 50 cm) served as excitation source. Fluorescence was detected at an angle of 90° through glass filters and a small monochromator (Jarrell Ash) with ca. 4 nm bandpass. A reference signal was obtained by directing part of the excitation light into a solution of rhodamine B in glycol serving as quantum counter. Fluorescence photons from the sample and the quantum counter were detected with photomultipliers (EMI 9659Q and EMI 9558Q) and counted by a multichannel analyzer (Canberra 8100) and a prescaler (Ortec), respectively. Fluorescence excitation spectra were obtained by scanning the excitation monochromator in 1.5 Å increments with a bandwidth of 2.5 Å. For fluorescence spectra the detection monochromator was stepped manually in 5 nm increments. The spectral sensitivity of the detection system was calibrated with a tungsten-halogen standard lamp (Optronic).

PMMA matrices for hole-burning experiments were created by casting a solution of PMMA and 3-hydroxyflavone dissolved in $CHCl_3$ onto a sapphire window. After evaporation of the solvent clear films of 300 μm typical thickness were formed. A pulsed dye laser (Lambda Physik FL 2002) pumped by an XeCl excimer laser (Lambda Physik EMG 100) was used for hole-burning. Absorption spectra before and after laser irradiation were taken with the light of a 75 W xenon arc lamp dispersed through a double-monochromator (Spex 1403, f = 85 cm). The intensities of the transmitted light and the reference beam were measured with the photon counting technique.

3. Results and Discussion

Argon matrices doped with 3-hydroxyflavone emit bright green fluorescence when exposed to UV-irradiation. The corrected quantum distribution spectrum (emitted quanta per wavenumber interval) of this emission is shown in Fig. 2. It consists of a dominant band peaked at 505 nm attributable to fluorescence from the tautomer form of 3-hydroxyflavone. At shorter wavelengths a weak emission is observed accounting for ca. 3% of the emitted quanta. The excitation spectra of these two emissions, monitored at 505 nm and 410 nm, are given as curves (a) and (b) in Fig. 2. Both excitation spectra show similar vibrational structure which is much better resolved than in organic glasses or PMMA matrices (compare, e.g., Fig. 5 below). However, the excitation spectrum of the violet fluorescence (curve b) is shifted almost 1000 cm^{-1} to lower wavenumbers compared to the excitation spectrum of tautomer fluorescence (curve a). Hence the violet emission stems not from the normal form of 3-hydroxyflavone, but must be due to molecules with a different ground state. These could be complexes with hydrogen bonding impurities. However, matrices made with a mixture of 4% water in argon show spectra almost identical to those in Fig. 2, with the violet emission increased to only 4.5%. Hence the formation of complexes seems to be inhib-

ited even when a large excess of water is present, presumably due to inhibited diffusion. We assign the violet emission to dimers or conformers of 3-hydroxyflavone which do not undergo ESIPT, probably because the OH-group forms no internal hydrogen bond. On the other hand, those molecules leading to the excitation spectrum (a) do not contribute a detectable amount of violet fluorescence but emit exclusively from the tautomer form. Elsewhere we have already reported that this tautomer fluorescence rises in less than 1 picosecond [17]. Hence it must be concluded that no barrier to ESIPT exists for unperturbed molecules of 3-hydroxyflavone in solid argon.

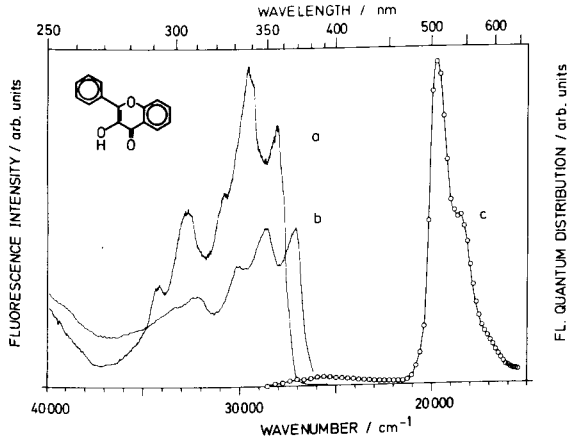

Fig. 2
Spectra of 3-hydroxyflavone isolated in solid argon at 15 K. (a): Excitation spectrum of the tautomer fluorescence monitored at 505 nm. (b): Excitation spectrum of the residual violet fluorescence monitored at 410 nm. (c): Corrected fluorescence spectrum (number of quanta per wavenumber interval) excited at 305 nm

The fluorescence and excitation spectra of 2,5-bis(2-benzoxazolyl)hydroquinone in solid argon at 15 K are shown in Fig. 3. The upper part of this figure refers to the dominant red emission from the tautomer, showing the excitation spectrum monitored at 585 nm and the fluorescence quantum distribution spectrum excited at the maximum of the excitation spectrum. The excitation spectrum shows two band systems of different character: A first band between 23000 cm^{-1} and 29000 cm^{-1} with broad vibrational structure, and a system of sharp vibronic bands between 29000 cm^{-1} and 34000 cm^{-1}. The diffuseness of the first band system indicates the coupling of the corresponding transition to low-frequency modes associated with the hydrogen bonds and ESIPT, which are known from the supersonic jet spectra [21, 22]. The second band system can be assigned to a transition which couples mainly to a few high-frequency modes. We assign these spectra to unperturbed molecules of 2,5-bis(2-benzoxazolyl)hydroquinone and conclude that in solid argon at 15 K these unperturbed molecules very rapidly undergo ESIPT leading with high yield to tautomer fluorescence.

In the search of fluorescence from the normal form a weak emission in the range 20000 cm^{-1} to 24000 cm^{-1} was observed. The excitation spectrum of this emission is shown in the lower part of Fig. 3. It shows two band systems similar to the excitation spectrum of the tautomer fluorescence, with diffuse and sharp character, respectively. Despite this similarity, both spectra are significantly different. The excitation spectrum of the blue fluorescence has slightly different vibrational structure and is red-shifted by ca. 400 cm^{-1} with respect to the excitation spectrum of the red fluorescence. The fluorescence quantum distribution spectrum excited at the maximum of the "blue" excitation spectrum, also shown in the lower part of Fig. 3, is mirror symmetric to the excitation spectrum and has only a small Stokes shift. (Some tautomer fluorescence is also observed since the large excess of unperturbed molecules has a small absorption at the excitation wavelength.) As in the case of 3-hydroxyflavone we assign the spectra associated with blue fluorescence to a dimer or conformer incapable of undergoing ESIPT. A possible structure could be one in which the benzoxazol-groups are rotated by 180° so that the hydrogen bonds are formed to the O-atoms instead of the N-atoms. From the absolute photon count rates we estimate that ca. 3% of the molecules are in the blue-fluorescing form.

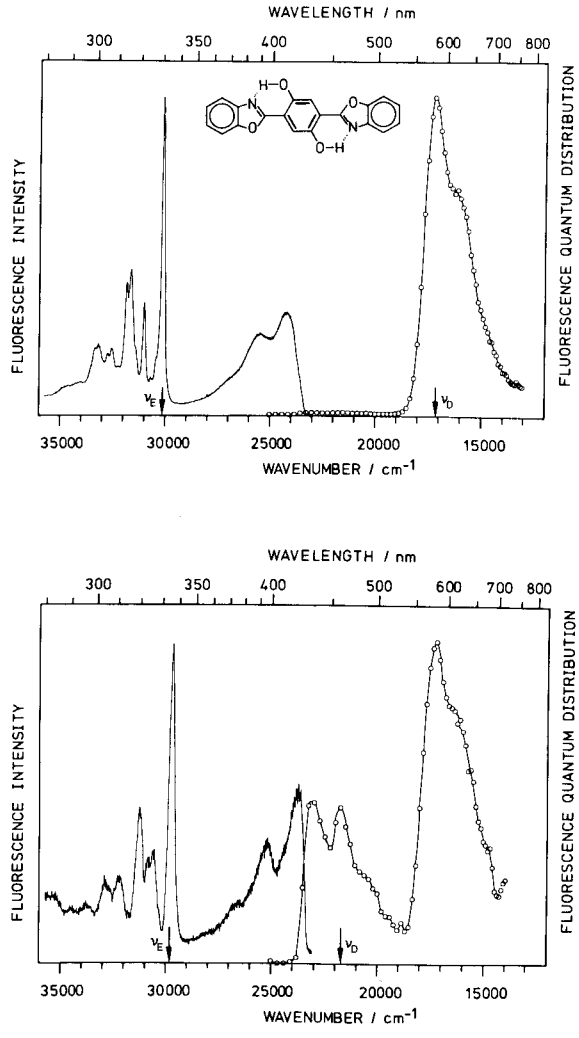

Fig. 3
Spectra of 2,5-bis(2-benzoxazolyl)hydroquinone isolated in solid argon at 15 K. Upper part: Corrected fluorescence spectrum of the tautomer form (right curve), and the excitation spectrum of the tautomer fluorescence (left curve). Lower part: Excitation spectrum and corrected fluorescence spectrum of the blue-fluorescing species. For discussion see text. Fluorescence spectra were excited at ν_E, and excitation spectra were detected at ν_D

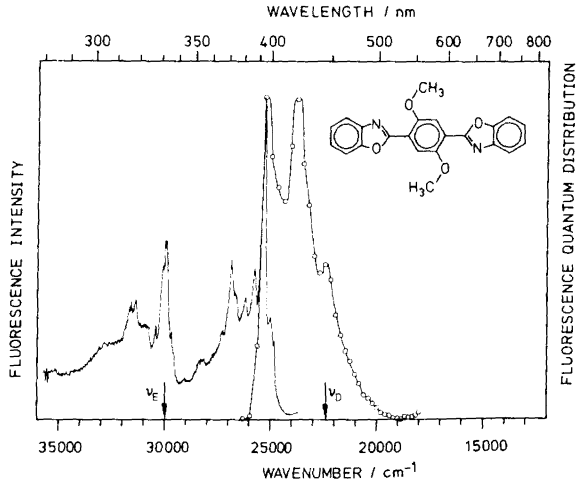

Fig. 4
Corrected fluorescence spectrum and fluorescence excitation spectrum of 2,5-bis(2-benzoxazolyl)-1,4-dimethoxy-benzene isolated in solid argon at 15 K

It is interesting to compare these spectra to those of the dimethoxyderivative shown in Fig. 4. In this molecule no ESIPT is possible, and only violet fluorescence is observed. In addition, the first band system of the excitation spectrum is no longer diffuse but shows vibrational finestructure. Some structure in the range where the excitation spectrum overlaps the fluorescence spectrum might indicate also site-structure or the existence of several conformers. Such drastic changes in the spectra with only minor modifications in the molecular structure support our assignment, that the spectra in the lower part of Fig. 3 are due to a dimer or conformer, and not caused by an impurity which has the hydrogen bonds blocked by some substituent.

As already mentioned, we found that the risetime of tautomer fluorescence is below 1 ps, too short to be resolved with a streak camera [17]. Such a fast process suggests the use of photochemical hole-burning to measure the homogeneous linewidth of the excited state undergoing ESIPT in order to gain indirect information on the decay time. However, both 3-hydroxyflavone and 2,5-bis(2-benzoxazolyl) hydroquinone were found to be absolutely stable against prolonged pulsed dye laser irradiation in argon matrices. (This fact also suggest that no barrier exists for proton back-transfer in the ground state.) However, the tautomer form of 3-hydroxyflavone is strongly polar and might react with other matrix materials. In fact, we observed partial bleaching of 3-hydroxyflavone in PMMA matrices at 10 K. Fig. 5 shows the absorption spectrum of 3-hydroxyflavone in PMMA before laser irradiation, and the change in optical density after laser irradiation at 365 nm. Although the difference spectrum is considerably narrower than the absorption spectrum, no prominent zero-phonon line is observed, prohibiting the interpretation of the spectrum in terms of a homogeneous linewidth. (For comparison, with tetraphenylporphin in the same matrix material narrow holes are easily observed with the same apparatus.) This is most probably due to the existence of low-frequency modes, whose spacing is much closer than the width of the inhomogeneous distribution. These modes are most probably connected with phenylring torsion. Hence the derivative lacking the phenyl group should be an interesting candidate for further investigations.

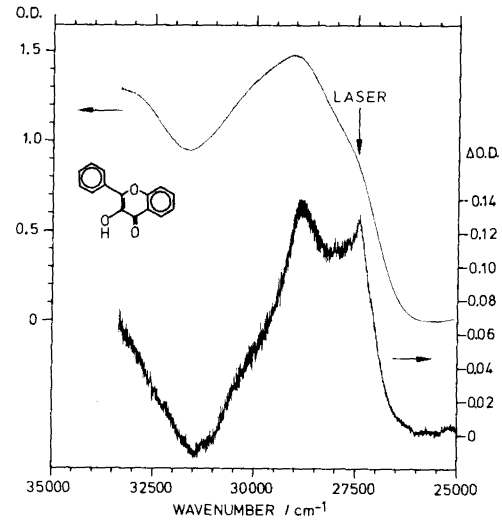

Fig. 5
Attempt of photochemical hole-burning of 3-hydroxyflavone in PMMA matrix at 10 K. Upper curve: Absorption spectrum (left scale). Lower curve: Change in optical density after laser irradiation at 365 nm (right scale)

4. Conclusions

The formation of complexes with external hydrogen bonds is strongly suppressed in argon matrices. The reason is that diffusion of hydrogen-bonding impurities like water is inhibited. Thus the majority of matrix-isolated molecules are unperturbed. The unperturbed molecules of 3-hydroxyflavone and 2,5-bis(2-benzoxazolyl)hydroquinone emit only fluorescence from their tautomer form, no emission from the normal forms could be detected. Hence ESPIT in these molecules shows no barrrier in argon matrices and occurs within 1 ps. Residual fluorescence ($< 3\%$) in the wavelength-range where the normal fluorescence is expected is due to molecules with a different ground state, presumably dimers or conformers lacking an internal hydrogen bond.

I thank Dr. B. Nickel for the loan of photon counting equipment. Helpful discussions with him and Dr. N. Ernsting are also acknowledge. The 2,5-bis(2-benzoxazolyl)hydroquinone was a kind gift of Dr. U. Brackmann, and its dimethoxyderivative was a gift of Dr. W. Kühnle. I am grateful to Prof. F. P. Schäfer and the Deutsche Forschungsgemeinschaft for support.

References

[1] A. Weller, Z. Elektrochem. *60*, 1144 (1956).
[2] W. Klöpffer, Adv. Photochem. *10*, 311 (1977).
[3] D. Huppert, M. Gutmann, and K. J. Kaufmann, Adv. Chem. Phys. *47*, 643 (1981).
[4] A. Weller, Progr. React. Kinet. *1*, 188 (1961).
[5] P. K. Sengupta and M. Kasha, Chem. Phys. Lett. *68*, 382 (1979).
[6] K. Smith and K. J. Kaufmann, J. Phys. Chem. *82*, 2286 (1978).
[7] J. Goodman and L. E. Brus, J. Am. Chem. Soc. *100*, 7472 (1978).

[8] W. Klöpffer and G. Kaufmann, J. Luminescence *20*, 283 (1979).
[9] D. Ford, P. J. Thistlethwaite, and G. J. Woolfe, Chem. Phys. Lett. *69*, 246 (1980).
[10] D. McMorrow and M. Kasha, J. Phys. Chem. *88*, 2235 (1984).
[11] O. A. Salman and H. G. Drickamer, J. Chem. Phys. *75*, 572 (1981).
[12] G. J. Woolfe and P. J. Thistlethwaite, J. Am. Chem. Soc. *103*, 6916 (1981).
[13] M. Itoh, K. Tokumura, Y. Tanimoto, Y. Okada, H. Takeuchi, K. Obi, and I. Tanaka, J. Am. Chem. Soc. *104*, 4146 (1982).
[14] A. J. G. Strandjord and P. F. Barbara, Chem. Phys. Lett. *98*, 21 (1983).
[15] A. J. G. Strandjord, S. H. Courtney, D. M. Friedrich, and P. F. Barbara, J. Phys. Chem. *87*, 1125 (1983).
[16] D. McMorrow, T. P. Dzugan, and T. J. Aartsma, Chem. Phys. Lett. *103*, 492 (1984).
[17] B. Dick and N. P. Ernsting, J. Phys. Chem. *91*, 4261 (1987).
[18] A. Mordzinski, A. Grabowska, W. Kühnle, and A. Krowczynski, Chem. Phys. Lett. *101*, 291 (1983).
[19] A. Mordzinski, A. Grabowska, and K. Teuchner, Chem. Phys. Lett. *111*, 383 (1984).
[20] A. Mordzinski and A. Grabowska, J. Mol. Struct. *114*, 337 (1984).
[21] N. P. Ernsting, J. Am. Chem. Soc. *107*, 4564 (1985).
[22] N. P. Ernsting, J. Phys. Chem. *89*, 4932 (1985).
[23] U. Brackmann, N. P. Ernsting, D. Ouw, and K. Schmitt, Chem. Phys. Lett. *110*, 319 (1984).
[24] A. Mordzinski and W. Kühnle, J. Phys. Chem. *90*, 1455 (1986).

Presented at the 86th Annual Meeting of the Deutsche Bunsen-Gesellschaft für Physikalische Chemie "Spektroskopie in kondensierten Phasen" in Göttingen, from May 28th – 30th, 1987 E 6548