

CALCULATION OF THE TOTAL DECAY OF ETHYNYLBENZENE AND SOME OF ITS DEUTERATED DERIVATIVES

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In this paper we present an absolute calculation of the radiationless decay of the lowest triplet state of ethynylbenzene and some of its deuterated derivatives. The rate constants were evaluated on the basis of Herzberg-Teller coupling. The absolute decay rates and the effect of deuterium substitution are in agreement with experiment within a maximum error of one order of magnitude. The distribution of the electronic energy among the accepting modes is discussed.

1. Introduction

In the preceding paper [1] we have studied the radiative properties of the lowest triplet state of ethynylbenzene. From both the calculated radiative decay constant and the experimental phosphorescence quantum yield, one must conclude that the observed total decay rate $k_{\text{tot}} = 1/\tau^p$ is mainly governed by the nonradiative channel.

The aim of this paper is to determine the absolute rate constant by calculating both the electronic matrix element $V_{S_0T_1}$ and the Franck-Condon factor FC. To this end we start with the golden rule formula (atomic units)

$$k_{S_0T_1} = \frac{2}{3}\pi \sum_{\nu} |\langle \chi_{S_0}^{\nu} | V_{S_0T_1} | \chi_{T_1}^0 \rangle|^2 \times \delta(E_{S_0,\nu} - E_{T_1,0}) \quad (1)$$

ν runs over the whole set of vibrational states of the ground state S_0 .

As shown in ref. [2] for the case of planar aromatic hydrocarbons the leading term is given by

$$k_{S_0T_1} = \frac{2}{3}\pi \sum_{p'} |V_{S_0T_1}^{p'}|^2 FC^{p'} \quad (2)$$

with

$$|V_{S_0T_1}^{p'}| = \partial \langle S_0 | \hat{H}_{so} | T_1 \rangle / \partial Q_{p'} |_{Q=0}$$

$$\begin{aligned} FC^{p'} &= \sum_{\nu} |\langle \chi_{S_0}^{\nu} | Q_{p'} | \chi_{T_1}^0 \rangle|^2 \delta(E_{S_0,\nu} - E_{T_1,0}) \\ &\approx \frac{1}{2\omega_{p'}} \sum_{\nu} |\langle \chi_{S_0}^{\nu} | \chi_{T_1}^0 \rangle|^2 \delta(E_{S_0,\nu} - E_{T_1,0} + \omega_{p'}) \\ &\approx (1/2\omega_{p'}) FC' \end{aligned}$$

The summation p' runs over all the possible promoting modes. In the case of a large energy gap we can split off nearly the whole contribution by the promoting mode [3] and end up with

$$\begin{aligned} FC' &= \exp(\kappa\omega_{p'}) FC \\ &(1/2\omega_{p'}) \exp(\kappa\omega_{p'}) FC \end{aligned}$$

FC denotes the usual Franck-Condon factor:

$$FC = \sum_{\nu} |\langle \chi_{S_0}^{\nu} | \chi_{T_1}^0 \rangle|^2 \delta(E_{S_0,\nu} - E_{T_1,0}) \quad (3a)$$

κ describes the slope in a logarithmic plot of FC versus the energy gap

$$\kappa = -\partial [\ln FC(E)] / \partial E |_{E=E_{T_1,0}} \quad (3b)$$

Table I
Electronic matrix elements

Compound	$ \tilde{V}_{S_0T_1^y} ^2$	$ \tilde{V}_{S_0T_1^z} ^2$	$ \tilde{V}_{S_0T_1^x} ^2$	$ \tilde{V}_{S_0T_1}^{\text{tot}} ^2$	k_z/k_y	$\frac{k_x}{k_z+k_y}$
C ₆ H ₅ CCH	0.271	0.078	0.005	0.354	3.45	0.014
C ₆ H ₅ CCD	0.274	0.079	0.005	0.358	3.49	0.014
C ₆ D ₅ CCH	0.151	0.052	0.004	0.207	2.90	0.020
C ₆ D ₅ CCD	0.159	0.054	0.004	0.217	2.97	0.019

Using approximation (3), we can rewrite eq. (2) in the usual form of the golden rule expression:

$$k_{S_0T_1} = \frac{2}{3}\pi |\tilde{V}_{S_0T_1}|^2 \text{FC},$$

with

$$|\tilde{V}_{S_0T_1}|^2 = \sum_{p'} |V_{S_0T_1}^{p'}|^2 \exp(\kappa\omega_{p'}) / (2\omega_{p'}). \quad (4)$$

2. Evaluation of the electronic matrix element

Since, in our case, we deal with a $\pi\pi^*$ -triplet state, we represent the corresponding wavefunction as a linear combination of singly-excited configurations ($^3\lambda_{\pi\pi^*}$):

$$|T_1\rangle = \sum_{\pi\pi^*} C_{\pi\pi^*}^{T_1} |^3\lambda_{\pi\pi^*}\rangle.$$

For the numerical evaluations of the electronic matrix elements $\partial \langle S_0 | H_{so} | T_1^{\tau} \rangle / \partial Q_p$, we use the approximation outlined in ref. [2]. Neglecting all multi-center spin-orbit integrals a reduction to integrals over AO's leads to:

$$\begin{aligned} \partial \langle S_0 | H_{so} | T_1^{\tau} \rangle / \partial Q_p = & \sum_{\pi\pi^*} C_{\pi\pi^*}^{T_1} \sum_{\tilde{q}k} (c_{\pi^*j} c_{\pi i} - c_{\pi j} c_{\pi^*i}) \\ & \times (2p_{x_j} | \partial / \partial Q_p | \sigma_k) \cdot S_{\sigma_k, 2p_{z_i}}^{-1} (2p_{z_i} | L^y | 2p_{x_i}) \\ & + \langle \pi^* | \partial L^y / \partial Q_p | \pi \rangle. \end{aligned} \quad (5)$$

A similar expression holds for $\tau = z$.

In eq. (5) $\sum_{\pi\pi^*}$ means the summation over all singly-ex-

cited configurations. $c_{\pi i}$ is the coefficient of the AO at center i in the MO π , σ_k an AO of σ -character, $S_{\sigma_k, 2p}^{-1}$ the reciprocal overlap matrix, L^{τ} the τ -component of the spatial part of the spin-orbit operator, and Q_p an out-of-plane vibration. The CI coefficients $C_{\pi\pi^*}^{T_1}$, the MO coefficients $c_{\pi i}$ and the matrix elements of $\partial / \partial Q_p$, L^{τ} , $\partial L^{\tau} / \partial Q_p$ over STO's are taken from the previous paper [2]. Using the numbers given there, we get the values for the matrix elements $|\tilde{V}_{S_0T_1}|^2$ tabulated in table 1. We like to point out that the variation of the total electronic matrix element $|\tilde{V}_{S_0T_1}^{\text{tot}}|^2$ amounts to 70%, when one goes from the all-protonated to the all-deuterated species. Furthermore, one sees by comparison with the partially deuterated species that this change is closely connected with the substitution of the ring hydrogens.

3. Evaluation of the Franck-Condon factor FC

For the evaluation of the Franck-Condon factor FC we use the expression derived by Fischer [4]:

$$\begin{aligned} \text{FC} = & (2/\pi)^{1/2} \{ \partial^2 \ln Z(t) / \partial t^2 \}_{t=t_s}^{-1/2} \\ & \times \{ Z(t_s) / Z(0) \} \exp(-E_{T_1,0} t_s), \end{aligned}$$

with

$$\begin{aligned} \ln Z(t) = & \sum_{\lambda, j} g_{\lambda j}^2 \{ \exp(i\lambda\omega_j t) [n(\lambda\omega_j) + 1] \\ & + \exp(-i\lambda\omega_j t) n(\lambda\omega_j) \}. \end{aligned}$$

n is the temperature-averaged occupation number. The saddle point t_s is determined by

Table 2
Coupling constants and energy distribution $E_{T_1} = 25\ 300$ (units: cm^{-1})

Normal mode	Coupling constant	Energy accepted (in cm^{-1})			
		$\text{C}_6\text{H}_5\text{CCH}$	$\text{C}_6\text{H}_5\text{CCD}$	$\text{C}_6\text{D}_5\text{CCH}$	$\text{C}_6\text{D}_5\text{CCD}$
$\equiv\text{C-H}$	$g_1^2 = 0.00924$ (0.01180)	620	340	790	450
$(\equiv\text{C-D})$	$g_3^2 = 0.000035$ (0.000070)	2890	760	5900	1680
$\omega = 3332(2610)$		} = 14%	} = 4%	} = 27%	} = 8%
$\phi\text{-H}$	$g_1^2 = 0.0462$ (0.06185)	2260	2420	1320	1490
$(\phi\text{-D})$	$g_3^2 = 0.000175$ (0.000350)	6500	7990	1940	5530
$\omega = 3067(2291)$		} = 36%	} = 42%	} = 13%	} = 29%
$-\text{C}\equiv\text{C}-$	$g_1^2 = 0.27$	3880	4070	4520	4360
$\omega = 2120$	$g_2^2 = 0.25$	3700	4040	4910	5440
		} = 31%	} = 33%	} = 38%	} = 40%
$\omega = 1601$ 	$g_1^2 = 0.400$	2710	2800	2960	3200
$\omega = 1192$ $\phi\text{-X}$	$g_1^2 = 0.36$	1260	1300	1300	1380
		} = 16%	} = 16%	} = 16%	} = 18%
out-of-plane	$g_2^2 = 0.1$				
$\omega = 750$		1100 = 4%	1150 = 5%	1260 = 5%	1400 = 6%
$\omega = 1200$	$g_2^2 = 0.025$				

$$E_{T_1} = \partial \ln Z(t) / \partial t |_{t=t_s}$$

$$= \sum_{\lambda j} \lambda \omega_j g_{\lambda j}^2 \{ \exp(\lambda \omega_j t_s) [n(\lambda \omega_j) + 1] - \exp(-\lambda \omega_j t_s) n(\lambda \omega_j) \}$$

The latter equation also allows one to estimate the relative importance of the individual normal modes for the nonradiative deactivation. The coupling constants are defined as

$$g_{1j}^2 = \frac{1}{2} M_j \omega_j [\Delta Q_j]^2,$$

$$g_{2j}^2 = [(\omega_j^{S_0} - \omega_j^{T_1}) / (\omega_j^{S_0} + \omega_j^{T_1})]^2,$$

$$g_{3j}^2 = x \omega_j / 30 \omega_j;$$

$x \omega_j$ is the cubic anharmonicity parameter. The uncertainty in the calculation of FC originates from the poor knowledge of the coupling constants $g_{\lambda j}^2$. Little or nothing is known about the geometry, the normal-mode frequencies, and the normal coordinates themselves in the excited states. From the analysis of high-re-

solution luminescence spectra, it was concluded [5], that in the case of benzonitril, the phenyl ring has a planar non-hexagonal structure in the lowest triplet state and is slightly expanded (hexagonal) in the first excited singlet state. For ethynylbenzene [6] the absorption spectra show that the mean increase in ring bond length on electronic excitation into S_1 (primarily localized on the benzene ring) is very close to that found for the corresponding benzene transition. Therefore, we treat the coupling constants $g_{\lambda j}^2$ as in benzene itself [7]. Those coupling constants, specific for the ethynyl-group, were determined on the basis of a modified PPP-type calculation [8]. The changes in the calculated bond orders were correlated semi-empirically with changes in bond length (g_{1j}^2) and normal-mode frequencies (g_{2j}^2). For the cubic anharmonicity parameter the value 9.2 cm^{-1} was chosen as suggested by Henry and Siebrand [9]. The set of parameters used is listed in table 2.

4. Discussion

From the experimental value of τ^P [10] (see table 3) one concludes that the nonradiative decay is about 1.5 times as fast in the per-protonated species as in the per-deuterated species. With respect to the lifetime substitution of the acetylenic hydrogen has about the same effect as substitution of all five ring-hydrogens. According to the model calculation, the nonradiative decay of the per-protonated system is about five times as fast as that of the per-deuterated species. Thus the discrepancy with the experimental value is large, but it is still smaller than one would ex-

pect from Siebrand's semi-empirical plot ($k_H/k_D \approx 300$). In agreement with Laposa's measurement, the rates for C_6H_5 CCD and C_6D_5 CCH are in size between those of the all-deuterated and all-protonated species, but they are, contrary to experiment, different from each other, C_6H_5 CCD having the higher ratio. A look at table 2 helps in understanding this general behaviour. Both in C_6H_5 CCH and C_6H_5 CCD the CH-stretching mode of the ring protons is the major energy sink. However, it accepts together with the acetylenic hydrogen or deuterium, respectively, not more than 50% of the total electronic energy to be converted, while in a "normal" unsaturated hydrocarbon about 80% of the total energy is accepted by the CH-stretching modes [11]. The remainder of approximately 50% goes mainly into the stretching of the triple bond (30%), and into skeletal and out-of-plane modes (20%). This latter fraction is nearly independent of the degree of deuterium substitution and is of that order of magnitude, which one usually finds in "normal" unsaturated hydrocarbons. We must therefore conclude that the acetylenic triple bond stretching mode runs in competition with the hydrogen stretching mode. Although the quanta of this mode are smaller by a factor of at least 2/3, if we consider that the main contribution of the hydrogen mode stems from the coupling through anharmonicities, the acetylenic triple bond compensates for this by having a much larger coupling constant. In the electronically excited state, the wavefunction is such that the bond order of the exocyclic triple bond is strongly reduced (and also the normal-mode frequency) and the bond length is increased. Naturally, these two facts are very helpful for achieving large Franck-Condon factors.

Table 3
Experimental and theoretical decay constants

	C_6H_5 CCH	C_6H_5 CCD	C_6D_5 CCH	C_6D_5 CCD	
$ \bar{\nu}_{S_0T_1}^{\text{tot}} ^2$	0.354	0.358	0.207	0.217	cm^{-2}
$(2\pi/3\hbar) \text{FC}$	1.48	1.12	0.51	0.30	$\text{cm}^2 \text{sec}^{-1}$
$k_{\text{nr}} = (2\pi/3\hbar) \bar{\nu}_{S_0T_1}^{\text{tot}} ^2 \text{FC}$	0.52	0.40	0.11	0.07	sec^{-1}
$1/\tau = k$ in 3MP	0.57	0.46	0.46	0.38	
in EPR	0.42	0.29	0.31	0.25	sec^{-1}

Generalizing this argument, we can conclude that in all molecules which contain an exocyclic double or triple bond, whose bond order is strongly influenced by an electronic excitation, a similar behaviour might be expected*. The amount of energy accepted by this very effective mode is even more increased, if the rest of the molecular system does not contain any other effective mode like the hydrogen stretching mode. Therefore, in the per-deuterated species, the acetylenic bond accepts 40% of the electronic energy to be converted, whilst the energy accepted by the deuterium stretching modes reduces to 37%. Furthermore, it is interesting to note that in C_6D_5CCH the one C-H stretching mode is capable of accepting twice as much energy as the five ring deuteriums. Comparing this compound with C_6H_5CCH one sees that the sum of the energy accepted by the ring- and acetylenic hydrogen and deuteriums respectively, is constant. Only the difference in distribution makes the radiationless decay in the all-protonated species so much faster.

From what is said above, one might perhaps try to use Siebrand's semi-empirical plot again, but with the following modification. The essential idea there is to determine the amount of energy accepted by the C-H and C-D stretching modes respectively. The value E_0 , which has to be subtracted from the actual energy gap can be interpreted as the energy accepted by all other modes (usually skeletal stretch and bending modes) [11]. If we add to the usual value of E_0 the amount of energy accepted by the acetylenic stretching mode, we can again determine the ratio of k_H/k_D . Using the adjusted energy differences, we end up with a ratio of $k_H/k_D \approx 10$ for the all-protonated and all-deuterated species, respectively.

5. Summary

In this paper we provided a model calculation of the nonradiative decay properties of ethynylbenzene and some of its deuterated derivatives. For the first

time, both the electronic matrix element and the Franck-Condon factor were evaluated starting from basic molecular parameters. The distribution of the energy among the accepting modes yields a clear understanding of the unusual deuterium isotope effect, which is observed experimentally. It is shown, that exocyclic multiple bonds, whose bond order changes strongly upon excitation, are very effective energy sinks. From this fact, one might conclude that reduction of the effectivity of the C-H vibrations in accepting energy by specific chemical substitution may lead to photochemical reactions with respect to the exocyclic bond.

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* Experimental evidence for such a behaviour has been found in the case of stilbene by Heinrich et al. [12]; styrene is under study in our laboratory. Preliminary results also show such an effect.