INTERSYSTEM CROSSING IN HEXAFLUOROBENZENE AND BENZENE VAPOURS. THE ROLE OF LOCAL MODES ON THE NONSTATISTICAL BEHAVIOUR OF BENZENE

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ABSTRACT — Previous work on decay of triplet states of aromatic molecules in the vapour phase is reviewed and the possible role of local modes in the decay of such systems is followed by studying triplet yields of C_6F_6 as a function of pressure and comparing the behaviour with that of C_6H_6. Measurements of the triplet yield of C_6F_6 using but-2-ene sensitized isomerization reveal that ϕ_T may show a weak increase (ca. 10 %) from pressures of 15 Torr ($\phi_T^\infty = 0.84 \pm 0.08$) down to 0.16 Torr ($\phi_T^0 = 0{,}92 \pm 0.08$). This behaviour contrasts with the strong decrease (4 times) observed in ϕ_T for C_6H_6 within the same pressure range. For C_6H_6 these observations are interpreted in terms of a nonstatistical intersystem crossing allowed by a slow intramolecular vibrational randomization process for the CH local modes, which are populated via a large electronic energy gap radiationless transition. The normal mode character of the CF stretches provides a faster intramolecular vibrational redistribution in T_1 and appears to be responsible for the statistical behaviour of C_6F_6. These features are supported by the vibrational energy dependence of hot triplet decay rates in protonated aromatic and heterocyclic molecules which are attributed to $T_1 \rightsquigarrow S_0$ transitions in the low energy region and to $T_1 \rightsquigarrow S_1$ transitions in the high energy region. The population of one CC promoting mode in the intersystem crossing process in C_6H_6 accounts for the small triplet yield in the isolated molecule. Comparison with the pressure dependence of triplet formation in protio - naphthalene and anthracene supports the view of a nonstatistical intersystem crossing from S_1 in these molecules.

1 – INTRODUCTION

Studies of the effect of pressure on the formation and decay of triplet states of aromatic molecules in the vapour phase may help to unravel the detailed fate of such molecules following optical excitation. Early work by Porter and Wright [1] on the flash photolysis of naphthalene and anthracene in the vapour phase noted a decrease in the amount of triplet (T_1) formed as the pressure of added buffer gas was reduced. Subsequent work by Porter and coworkers [2] using better experimental conditions confirmed these previous findings for a pressure region between 0.05 to 10 Torr. With the advent of laser flash photolysis relevant work was carried out to elucidate the mechanism of the population of triplet states via intersystem crossing (i. s. c.) from S_1 [3-6]. However, it is only recently that molecular beam with multicolor photoionization techniques has allowed the direct observation of triplet states under isolated conditions at several energies of excitation [7-11]. Smalley and coworkers have found that the vibrational energy, E_v, dependence of the hot triplet, T_1^v, decay rates in pyrazine, pyrimidine [10], toluene [9], benzene [8, 11] and naphthalene [7] is very strong at low energies (S_0 region), but becomes very weak at high energies, when the total energy is larger than the electronic energy of S_1 (S_1 region) . In each region the relation between the triplet decay rates and E_v is virtually exponential, but the intercept at $E_v = 0$ in the S_1 region is 3 to 5 orders of magnitude higher than the intercept in the S_0 region. Such vibrational energy effects were initially interpreted by considering that the T_1 decay was only caused by i. s. c. to S_0 . A dilution of the good acceptor modes due to a fast intramolecular vibrational relaxation (IVR) was responsible for the weakening of the dependence of $k_{T_1^v \rightsquigarrow S_0}$ at high E_v [9]. However recently Smalley and coworkers [12] have shown that this saturation effect of i. s. c. at high energies cannot be explained by a radiationless transition $T_1^v \rightsquigarrow S_0$ associated with IVR .

Pyrazine and pyrimidine have long been recognized as examples of molecules in the intermediate coupling situation [13, 14] for $S_1 \rightsquigarrow T_1$. This i. s. c. can be represented kinetically by a reversible process [15]

$$\begin{tikzcd} S_1 \arrow[r, shift left, "k_T"] \arrow[d, "k_i"'] & T_1^{v'} \arrow[l, shift left, "k_S"] \arrow[d, "k_j"] \\ {} & {} \end{tikzcd}$$

where k_i and k_j are the rates of irreversible and k_T and k_S are the rates of reversible crossing. The vibrationally hot $T_1^{v'}$ state, upon a short pulse excitation in S_1, rises with a first order rate constant λ_1 and decays with a rate constant λ_2

$$2\lambda_{1,2}=k_i+k_T+k_j+k_S \pm [(k_i+k_T-k_j-k_S)^2 + 4k_Tk_S]^{1/2} \qquad (1)$$

In molecules such as pyrazine and pyrimidine $k_i+k_T-k_j-k_S >> (4k_Tk_S)^{1/2}$ and consequently $\lambda_2 \simeq k_S+k_j$; in the isolated molecules k_j is very small and $\lambda_2 \simeq k_S$. Consequently the triplet decay rates in the S_1 region can be attributed to the i. s. c. $T_1^{v'} \rightsquigarrow S_1$, whereas at lower vibrational energies the triplet decay is due to $T_1^{v} \rightsquigarrow S_0$. This would explain why the intercept of the triplet decay rates in the S_1 region in $3 - 6 \times 10^3$ times larger than the cold triplet decay rate [10]. The dependence of the decay rates on E_v depends on the electronic energy gap between the states involved in the transition [14]. For small electronic energy gaps, as is the case for a $S_1 \rightsquigarrow T_1$ process it is a weak dependence, while for a large electronic energy gap as in the $T_1 \rightsquigarrow S_0$ process it is a strong dependence.

Owing to the similarity in the dependence of the triplet decay rates with E_v of benzene [8, 11] toluene [9] and naphthalene [7] and the above mentioned heterocyclic molecules, the same interpretation is foreseeable for these aromatic molecules. The pressure dependence of triplet formation of benzene [16, 17], naphthalene [2, 5], anthracene [2, 4, 6] and acridine [18] has been extensively studied by several authors and nonstatistical behaviour has been claimed for the i. s. c. process from S_1 [2, 6, 17, 18]. Strong support for such a claim comes from recent molecular beam experiments which allowed the observation of quantum beats in the fluorescence decay of anthracene [19] when excited into several levels in S_1. Previously such effects have only been observed in much smaller molecules, pyrimidine, biacetyl and methylglyoxal [20, 21], classified as intermediate case molecules with respect to i. s. c. from S_1.

For radiationless transitions between two electronic states, a nonstatistical behaviour requires that the density of coupled levels in the final state is comparable to that in the initial state. For the i. s. c. process $S_1 \rightsquigarrow T_1$ in aromatic molecules a suggestion was made that such a low density of states can only be provided by the CH vibrational levels [18] which are good accepting modes for the nonradiative transition $S_1 \rightsquigarrow T_1$ and which have a strong local mode character [22-24]. Such local modes interact strongly between themselves, but are weakly coupled with the bath of normal modes [24, 25]. In these conditions the intramolecular vibrational redistribution process into the quasi-continuum bath of the normal modes is slow and can determine the rate of the overall nonradiative transition. In contrast normal modes are strongly coupled with their own bath and provide a fast redistribution of vibrational energy. To investigate the role of local and normal modes on i. s. c. we decided to study the effect of pressure on the triplet yield of C_6F_6 and compare it with the well established behaviour of the C_6H_6 triplet state [16, 17]. C_6F_6 is a convenient molecule, because it has the same size as benzene, has stretching modes (CF) with a normal mode character [23, 24] and an electronic $S_1 - T_1$ energy gap ($\sim 9500\ \mathrm{cm}^{-1}$) that is virtually identical to that of C_6H_6, judging from the fluorescence [26] and phosphorescence spectra [27].

2 – EXPERIMENTAL

Spectrograde perfluorobenzene (Aldrich) was employed and its purity, checked by vapour phase gas chromatography, was 99 %. Cis-butene (Fluka) had a percentage of trans-butene of 0.3 %. Mixtures of C_6F_6 and cis-butene were prepared on a mercury-free vacuum line and spectroscopically pure argon (Air-Liquide) was added to increase the overall pressure. Samples were irradiated with a 150 W medium pressure Hg-lamp on a wavelength region between 250-260 nm. Absolute yields were determined on irradiation at 260 ± 1 nm by a 250 W xenonlamp through a monochromator. Analysis of reactants and products was carried out on a Perkin-Elmer 900 gas chromatograph with columns filled with Durapak. The percentage of isomerization was always $\leqslant 1$ %. Further experimental details are given elsewhere [17].

3 – RESULTS

The triplet yield of C_6F_6 measured by cis-but-2-ene isomerization was found to decrease by 10 % upon addition of argon, to a pressure of 15 Torr. At the low concentrations of butene used not all the triplet states were scavenged, but the fraction of triplets quenched by cis-butene was constant throughout the whole pressure range, because the same mixture of C_6F_6 and cis-butene (0.08 Torr C_6F_6 + 0.08 Torr cis-butene) was employed in all the experiments.

To determine absolute triplet quantum yields a pressure of cis-butene > 100 Torr is required to ensure the scavenging of all the triplet molecules [27]. Mixtures of 0.08 Torr C_6F_6 and cis-butene, with pressures of 100 Torr and 400 Torr, were employed. The quantum yield of isomerization was 0.18 and 0.38 respectively. Assuming that all triplets are scavenged at 400 Torr of butene, an absolute yield of $\overset{\infty}{\phi_T} = 0.84 \pm 0.08$ is estimated from the stationary state ratio $[\text{t-Bu}]_s / [\text{c-Bu}]_s = 2.2$, determined for C_6H_6 at high pressures [17]. The small increase in the yield of triplet with a decrease in pressure ($\phi_T^0 = 0.92 \pm 0.08$) is in agreement with the small decrease in the fluorescence yield with pressure, attributed to vibrational relaxation in S_1 [27]. The fluorescence yield from the thermally equilibrated S_1 state is $\overset{\infty}{\phi_F} = 0.019 \pm 0.001$ and, consequently, triplet and fluorescence yields do not add up to unity (0.86). In the isolated molecule, upon excitation at 260 nm, $\phi_F^0 \simeq 0.005$ [27] and $\phi_T^0 + \phi_F^0 \simeq 0.93$.

4 – DISCUSSION

Intramolecular Vibrational Relaxation

The contrast between the pressure dependence of C_6F_6 and C_6H_6 triplets is illustrated in Fig. 1. The latter shows a nonstatistical behaviour whereas the former behaves statistically with respect to i.s.c.. C_6F_6 and C_6H_6 differ through few electronic and vibrational features. Electronically the presence of lone pair electrons in C_6F_6 can increase spin-orbit coupling and this can explain why $\overset{\infty}{\phi_T}$ is higher in this molecule than in C_6H_6. However such differences in spin-orbit coupling do not affect the relative yields as a function of pressure. The different behaviour of the two molecules should be attributed to differences in the CF and CH stretching modes. In principle the lower frequency of CF modes, compared to CH modes, increases the density of states for the triplet manifold and could place C_6F_6 in the statistical case.

However, molecules such as toluene, naphthalene and anthracene possess much higher density of states and they behave also in a nonstatistical fashion. Consequently we attribute the observed differences to the local mode character of the CH stretches in contrast with the normal mode character of the CF stretches [23, 24].

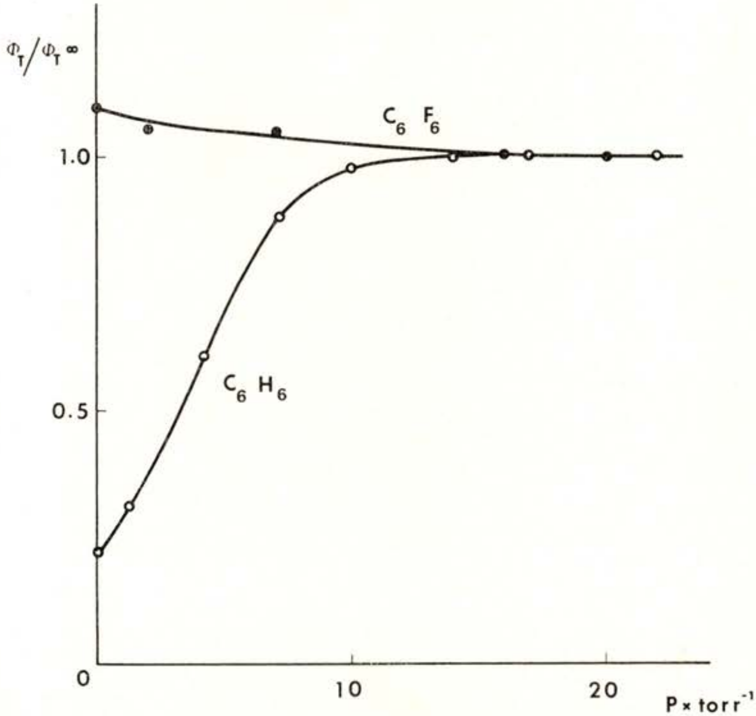

Fig. 1 — Relative triplet yields of C_6H_6 (o) and C_6F_6 (•) as a function of the pressure of added argon (0.05 Torr C_6H_6 + 0.05 Torr cis-butene; 0.08 Torr C_6F_6 + 0.08 Torr cis-butene)

On the basis of deuterium isotope effects [14] in aromatic hydrocarbons, one finds that the CH stretching modes participate significantly as accepting modes for electronic energy gaps $\gg 5000\ \text{cm}^{-1}$ and become the main accepting modes for electronic energy gaps $\gg 10\,000\ \text{cm}^{-1}$. In C_6H_6 the electronic energy gap $S_1 - T_1$ is close to 10 000 cm^{-1} and considering that one CC promoting mode is populated, ca 75 % of the vibrational energy will go into the CH stretches after i. s. c. to T_1 [27]. A similar situation is expected in naphthalene and anthracene where the electronic energy gaps $S_1 - T_1$ are even larger.

IVR of highly vibrational CH overtone excitation in C_6H_6 vapours has been studied by Berry and coworkers [29, 30]. Vitrational relaxation is a very fast process (50-200 fs) but is highly nonstatistical. Example of such behaviour is the nearly constant bandwith in CH overtones over a vibrational energy range (up to 10 ν_{CH}) that involves 6 orders of magnitude change in the vibrational density of states. Deuteration also does not affect the overtone relaxation. These studies reveal that IVR proceeds via specific state-to-state intramolecular processes, producing a limited subset of final vibrational levels of CH stretches and possibly CH bending modes. Coupling to the bath of normal modes is a relatively slow process [25]. Evidence for the slow rate of such a relaxation process in other aromatic molecules with CH modes is given by the T - T absorption spectra of hot triplet species. Owing to the fairly restricted Franck-Condon factors governing i. s. c., only a few vibronic states are initially populated in $T_1^{v'}$ and its absorption is more structured than that of the relaxed state. Such a feature is quite evident for the nascent triplets of naphthalene [5] and anthracene [6] observed on a nanosecond time scale. In contrast normal modes such as the CF modes are strongly coupled between themselves and can very quickly populate a great manifold of vibrational levels [25] in C_6F_6 (T_1) following i. s. c. . Studies [31] of IVR in naphthalene optically populated in a few normal modes reveal that intramolecular redistribution of energy is fast and it occurs within an order of magnitude, to the bath of all the vibrational levels.

Using the concept [32] of the number of coupled states, N, and its relationship with the density of states, ρ, it can be shown that

$$N_T / N_S \simeq \rho_T k_T / (\rho_S k_S) \qquad (2)$$

Eq. (2) reveals that the weak exponential vibrational energy dependence of the triplet decay rates in the S_1 region reflects the similar dependence of the S_1 decay rates. In order to test eq. (2) in pyrimidine we have partitioned, as usual, the vibrational modes of the molecules in S_1 and T_1 states into sets which will be treated as degenerate, with frequencies 500, 1000, 1500 and 3000 cm^{-1}. The density of states was calculated by the Haarhoff [33] equation and compared with ρ_T / ρ_S calculated through eq. (2). For such calculation the number of coupled states was estimated by direct counting, considering all possible numbers of quanta which add up to the correct energy. Table 1 presents the calculations and reveals that a fair agreement (within an order of magnitude) was found when all the vibrational modes were considered for the transition rather than just the CH stretches. Similar results were found for pyrazine. For both molecules the electronic energy gap is small (ca 2000 cm^{-1}) and CH modes are not good accepting modes. A different situation occurs for large electronic energy gap transitions. Considering the decay of the hot triplets $T_1^{v'}$ in benzene and toluene reported by Smalley and coworkers as a measure of the average k_S rates [34], ratios of density of states can also be calculated. Table 1 shows the results and in contrast with the findings for the heterocyclic molecules a fair agreement can be found if the CH local stretches were almost the only modes involved in the i. s. c. process $S_1 \rightleftharpoons T_1$. This supports the view that the nonstatistical behaviour of benzene and other aromatic molecules is due to the strong local character of the CH modes.

Triplet Yields

The pressure dependence of triplet formation in large molecules has been currently interpreted in terms of two kinds of mechanisms. One considers the i. s. c. process $S_1 \rightsquigarrow T_1$ in the statistical situation, but proposes the existence of a fast (<100 ns) i. s. c. process from the hot triplet to the ground state [5, 16]. The other considers a pressure dependent i. s. c. process such as in the intermediate coupling situation [2, 4, 6, 17].

Observations of triplet formation, at low pressures, immediately following i. s. c. can provide a clear distinction between these two kinds of mechanisms [5]. Within the fast $T_1^{v} \rightsquigarrow S_0$ i. s. c. mechanism the triplet concentration should decrease with time, on a nanosecond scale. Since such a decrease corresponds to the rapid loss of the high triplet levels to S_0, it should be numerically

TABLE 1 — Ratio of density of states in the Intersystem Crossing Process $S_1 \rightsquigarrow T_1$ of Heterocyclic and Aromatic Molecules.

Molecule	Vibrational Modes E/cm^{-1}	g	E_S/cm^{-1}	E_I/cm^{-1}	k_T/s^{-1}	k_S/s^{-1}	N_I/N_S		ρ_T/ρ_S					
									all modes		CH modes		n CH and 1 CC modes	
							all modes	CH modes	Haarhoff	eq. (4)	Haarhoff	eq. (4)	Haarhoff	eq. (4)
Pyrimidine	500 1000 1500 3000	6 (*b*) 9 5 4	0	2543	(*a*) 3.7×10^8	(*b*) 1.8×10^6	2.9×10^3	1	31	14	2.9	0.005	—	—
Pyrazine	500 1000 1500 3000	6 (*b*) 9 5 4	0	4056	(*c*) 2×10^9	(*b*) 3.4×10^6	6×10^4	35	182	100	4.9	0.06	—	—
Benzene	500 1000 1500 3000	6 (*f*) 12 6 6	550	9500	(*d*) 9×10^6	(*d*) 1×10^6	7×10^5	126	92	1×10^5	37	14	230	240
Toluene	500 1000 1500 3000	8 (*f*) 14 8 8	0	8600	(*e*) 8.5×10^6	(*e*) 3.5×10^5	4×10^7	330	3×10^4	1×10^6	44	13.5	350	300

(*a*) Reference [32]; (*b*) Reference [10]; (*c*) A. Frad, F. Lahmani, A. Tramer and C. Tric, *J. Chem. Phys.*, (1974), **60**, 4419; (*d*) Reference [8] and [34]; (*e*) Reference [9]; (*f*) C. La Lau and R. G. Snyder, *Spectrochim. Acta.* (1971), **27A**, 2073; CH_3 torsion was not included.

identical to the increase in ϕ_T of the relaxed triplet from low to high pressures. Studies of the triplet absorption spectra of anthracene (3 Torr CH_4) by nanosecond laser flash photolysis, as a function of time, reveal the opposite effect since the triplet concentration increases by a factor of 1.25 times ca. 1 μs after excitation [4, 6]. Schröder et al. [5, 35] have carried out identical studies for naphthalene at low pressures (0.07 Torr) and have found that the integrated triplet absorption decreases by a factor of 1.8 with an increase in time, a value close to the overall increase of ϕ_T (2.0 times) from low to high pressures. However the integrated absorption bands at shorter and longer times did not correspond to the same vibrational bands. When this situation is properly taken into consideration we can conclude that at most only 15 % of naphthalene triplets are lost via a $T_1^v \rightsquigarrow S_0$ process. Consequently these experimental studies support also the view that naphthalene and anthracene triplets behave nonstatistically.

Benzene [17], naphthalene [36] and anthracene [4] have small but significant triplet yields under isolated conditions. The relative triplet yields are virtually identical for these molecules $\overset{o}{\phi}_T / \overset{\infty}{\phi}_T = 0.25$. In C_6D_6 this yield decreases, $\overset{o}{\phi}_T / \overset{\infty}{\phi}_T = 0.17$. These yields can be attributed mainly to the irreversibility in the i. s. c. $S_1 \rightsquigarrow T_1$ owing to the direct population of a CC promoting mode which has a normal mode character. Under the experimental excitation conditions the energy in T_1 is $E_v = 10\,000\ cm^{-1}$ to $12\,000\ cm^{-1}$ for C_6H_6, $C_{10}H_8$ and $C_{14}H_{10}$ and consequently in the nonradiative transition 1 CC ($\nu_{CC} \simeq 1500\ cm^{-1}$) and 3 CH ($\nu_{CH} \simeq 3000\ cm^{-1}$) modes are populated. Assuming that the ratio of triplets that would not revert to S_1 is proportional to the population of the CC modes, 25 % of the triplets formed will not come back to S_1 and this is in good agreement with the experimental ratio $\overset{o}{\phi}_T / \overset{\infty}{\phi}_T = 0.25$. In C_6D_6 the i. s. c. populates 1 CC an 4 CD modes ($\nu_{CD} \simeq 2100\ cm^{-1}$) in the T_1 state, leading to 20 % of irreversibility. This value is also close to the experimental ratio $\overset{o}{\phi}_T / \overset{\infty}{\phi}_T$ (C_6D_6) = 0.17. Better agreement between the ratio of states was achieved for benzene and toluene when the population of a CC promoting mode was considered (Table 1).

Pressure dependent fluorescence yields and decays were found for C_6H_6 and $C_{10}H_8$ [17, 37], and agree with the pressure dependence of triplet yields. With anthracene [6] pressure dependence was also found for the fluorescence intensity, but the fluorescence decay is exponential. We have attributed such a feature to the irregularities in the spacing and coupling constants in the $S_1 \rightsquigarrow T_1$ transitions which can lead to a variety of k_S rates. In this situation the fluorescence decay, mixture of a manifold of biexponential decays, was shown [6] to be pressure independent with a rate equal to $k_i + k_T$. However the observation of quantum beats [19] in the fluorescence of anthracene reveal that under proper experimental conditions pressure effects on the fiuorescence decay can be observed.

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[35] SCHRÖDER et al. [5] have found that the $\overset{v}{T_1}$ absorption, in the observation region $\lambda \gg 380$ nm, is red shifted with respect to the relaxed state T_1. The spectral T - T absorption area of $\overset{v}{T_1}$ between 380 nm and 420 nm decreased with time by 1.8 times. However this spectrum includes two band progressions (408 nm and 390 nm) whereas for the equilibrated spectrum only one band (397 nm) was considered. The 390 nm band at low pressures corresponds to the second band (377 nm) at high pressures (see the high pressure spectrum reported in ref. [1]; there is a misprint in the second band, ν (cm^{-1}) = 26,546 cm^{-1}). Since to estimate relative concentrations we have to compare the same bands in spectra, the relevant ratios of areas, A ; are $A_{408} / A_{397} \simeq 1.18$ or $(A_{408} + A_{390}) / (A_{397} + A_{377}) \simeq 1.13$: These factors are too low to explain the increase in ϕ_T by a factor of 2.0 upon addition of 2.5 Torr of argon. So the net increase in triplet concentration is 1.7.

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