On the Relationship Between the Rates of the Radiative and Radiationless Deactivation of the Lowest Triplet State of Aromatic Compounds

Maximilian Zander
Rütgerswerke AG, Castrop-Rauxel

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For groups of structurally related aromatic compounds with similar T_1-S_0 energy gap linear correlations exist between the rate constants of the radiative and radiationless $T_1 \rightarrow S_0$ transition. Significant exceptions may indicate further radiationless deactivation processes originating in T_1 in addition to $T_1 \rightarrow S_0$ intersystem crossing.

1. Introduction

Orlandi and Siebrand [1] have shown that radiationless transitions in molecules are subject to an electronic propensity rule which does not refer directly to the states involved in the transition but instead to the radiative transition with which it competes. In a series of related molecules higher radiative rate constants are accompanied by higher rate constants for the competing radiationless transition, i.e. radiative and non-radiative rate constants are to some degree correlated. Since the Orlandi-Siebrand rule operates independently of the Franck-Condon principle, application of the rule first requires elimination of Franck-Condon effects, e.g. by extrapolating rate constants to zero energy gaps [2].

In this note the Orlandi-Siebrand rule is examined with regard to the $T_1 \rightarrow S_0$ transition of some aromatic compounds with the intention to contribute to the evaluation of the rule as a heuristic principle in molecular triplet spectroscopy.

2. Results and Discussion

The compounds selected for this study are listed in Figure 1. Their T_1-S_0 energy gaps (phosphorescence 0.0 bands measured in solid glasses at 77 K; π, π^* phosphorescence in all cases) lie in the narrow range from 19 750 to 21 000 cm^{-1}. Rate constants of the radiative (k_{PT}) and non-radiative (k_{GT}) $T_1 \rightarrow S_0$ transitions were taken from the references given in Figure 1.

In Fig. 2 k_{GT} is plotted against k_{PT} for the 17 compounds studied. The values for 1-methylnaphthalene (**1**), 1,1′-binaphthyl (**2**) and halogen derivatives **3**–**5** and **12**–**15** fit the straight line **a** (correlation coefficient $r = 0.9870$) while the values for carbonyl derivatives **6, 7, 9,** and **10** fit the straight line **b** ($r = 0.9597$).

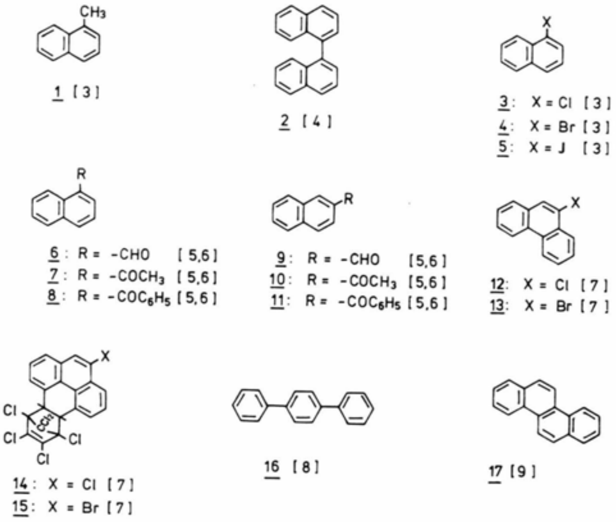

Fig. 1. Compounds studied. Numbers in brackets refer to references from which k_{PT}, k_{GT} and $\Delta E(T_1-S_0)$ data (77 K) were taken.

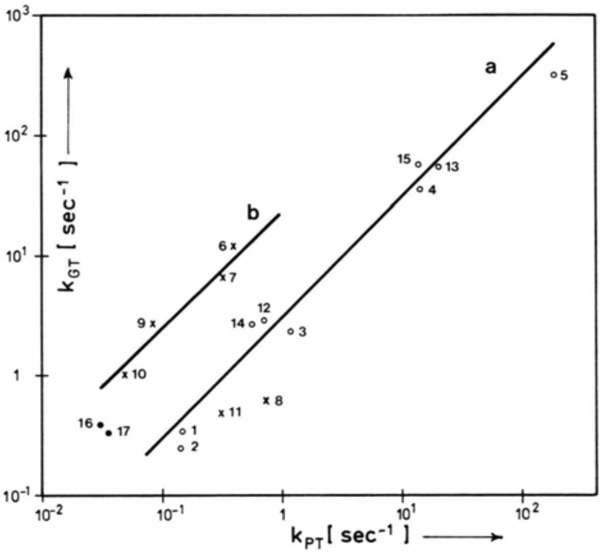

Fig. 2. Plot of the rate constants of non-radiative (k_{GT}) vs. radiative (k_{PT}) transitions (numbers refer to compounds given in Figure 1). Circles: 1-methylnaphthalene (**1**), 1,1′-binaphthyl (**2**), halogen derivatives of naphthalene and phenanthrene. Crosses: carbonyl derivatives of naphthalene. Points: p-terphenyl (**16**), chrysene (**17**).

Though the trend of the results is in accordance with the Orlandi-Siebrand rule it is quite obvious that different structural features lead to different relationships and considerable scatter. It is very likely that the main reasons are: (i) Approximately identical T_1-S_0 energy gaps do not guarantee that the Franck-Condon factors governing the $T_1 \rightarrow S_0$ transition are also very similar if different types of compounds are compared, (ii) k_{PT} and k_{GT} values were derived from experimental data on the assumption that intersystem crossing (ISC) from the S_1 state to the triplet manifold is the only

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Reprint requests to Professor Dr. M. Zander, Rütgerswerke AG, D-4620 Castrop-Rauxel, FRG.

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non-radiative deactivation path of the S_1 state. However, in cases where $S_1 \rightarrow S_0$ internal conversion is not negligible, true k_{PT} values are larger and true k_{GT} values are smaller compared to experimental values.

Furthermore, it has to be taken into account that the effect of spin-orbit coupling on k_{PT} and k_{GT} may be different in planar compared to non-planar compounds [10, 11]. As follows from inspection of Stuart-Briegleb molecular models, deviation from planarity is much larger in compounds **8** and **11** compared to all other carbonyl derivatives studied. This may possibly provide an explanation that the values for **8** and **11** do not fit the straight line **b** whereas it is probably accidental that they lie close to straight line **a**.

The Orlandi-Siebrand rule cannot be applied to the $T_1 \rightarrow S_0$ transition in cases where $T_1 \rightarrow S_0$ ISC is not the only non-radiative route through which the T_1 state is depopulated. Conversely, exceptions from the rule may sometimes indicate the occurrence of additional routes. An example (monobromo[2.2]paracyclophane [12]) has been recently discussed. N-Vinylcarbazole (NVC) provides a further example.

While the $T_1 - S_0$ energy gap is very similar in NVC and carbazole or N-alkylcarbazoles, the phosphorescence quantum yield ϕ_p of NVC differs markedly from that of carbazole (N-alkylcarbazoles) (ϕ_p (carbazole) $= 0.2$ [13], ϕ_p (NVC) $< 1 \cdot 10^{-4}$ [14, 15]). However, it has been shown [16] (i) that $S_1 \rightarrow T_n$ ISC rates of NVC and N-alkylcarbazoles are comparable and (ii) that NVC and N-alkylcarbazoles sensitize the naphthalene phosphorescence (by intermolecular triplet-triplet energy transfer) to the same extent. The rate constant of intermolecular T–T energy transfer from carbazole [17] or N-ethylcarbazole [15] to naphthalene amounts approximately to $0.3\,\text{sec}^{-1}$. From these observations it is concluded that the triplet lifetime τ_p of NVC is > 1 sec but does probably not exceed τ_p of carbazole (N-alkylcarbazoles), i.e. NVC is assumed to have a triplet lifetime between 1 and 10 sec. The quantum yields ϕ_T of triplet formation of NVC and carbazole (N-alkylcarbazoles) are also very similar [15, 16]. With ϕ_T (NVC) ≈ 0.5 as estimated for carbazole [13] it follows according to

$$\phi_P = \phi_T \, k_{PT} \, \tau_P = \frac{\phi_T}{1 + k_{GT}/k_{PT}}$$

that k_{PT} (NVC) is in the range 10^{-4}–$10^{-5}\,\text{sec}^{-1}$ and correspondingly k_{GT} (NVC) in the range 1–$10^{-1}\,\text{sec}^{-1}$. The figures for carbazole are: $k_{PT} \approx 4 \cdot 10^{-2}\,\text{sec}^{-1}$, $k_{GT} \approx 1 \cdot 10^{-1}\,\text{sec}^{-1}$ [13].

However, according to the Orlandi-Siebrand rule k_{GT} (NVC) should be much smaller than k_{GT} (carbazole). Thus the observed result may indicate that in NVC in addition to $T_1 \rightarrow S_0$ ISC a further radiationless deactivation route originating in T_1 is effective which does not occur in carbazole and N-alkylcarbazoles.

In conclusion, application of the Orlandi-Siebrand rule may be regarded as a useful means to detect cases where $T_1 \rightarrow S_0$ ISC is not the only radiationless deactivation route of the T_1 state though further experiments are always needed for the identification of these additional routes.

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