Note on the Influence of External Heavy-Atom Perturbers on the Phosphorescence Spectrum of Triphenylene

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Spectral changes in symmetry-forbidden phosphorescence spectra observed in the presence of external heavy-atom perturbers may have quite different causes depending on the chemical nature of the perturber. This is exemplified using triphenylene as the phosphorescent compound and methyl iodide and silver perchlorate respectively as the perturber. Intensification of the 0-0 band of the symmetry-forbidden phosphorescence spectrum of triphenylene by silver perchlorate is assumed to result from symmetry-reduction of the hydrocarbon by ground-state complex formation with silver perchlorate.

The radiative $T_1 \rightarrow S_0$ transition of triphenylene is both spin- and symmetry-forbidden [1]; correspondingly, the intensity of the 0-0 band (427 nm) in the phosphorescence spectrum of triphenylene is very low (Fig. 1, curve a; ethanol, 77 K). External heavy-atom perturbers, e.g. methyl iodide, enhance strongly the intensity of the 0-0 band [2, 3]. This is due to a second-order mixing of perturber singlet-state character into the T_1 state of the phosphorescent molecule [4]. As associative forces between the perturber and the aromatic hydrocarbon are negligible perturber and aromatic molecules are randomly distributed in the rigid matrix. On the contrary, silver salts, e.g. $AgClO_4$, as external heavy-atom perturbers form ground-state complexes with aromatic hydrocarbons [5] that are well-defined regarding stoichiometry and geometry. In many cases these ground-state complexes are phosphorescent [6, 7, 8]. The subject of the present communication is a comparative study of the influence of methyl iodide and $AgClO_4$ respectively as external heavy-atom perturbers on the phosphorescence spectrum of triphenylene in ethanol at 77 K.

As a measure for the external heavy-atom effect the ratio of intensities of the 0-0 band (427 nm) to the band at 460 nm which is the most intense band in the unperturbed spectrum was used (Fig. 1, curve a). This ratio ($R_I = I_{427}/I_{460}$) is 0.1 in the unperturbed spectrum. The dependence of R_I on the perturber concentration (CH_3J, $AgClO_4$) is shown in Figure 2. While the maximum R_I value is 1.5 if CH_3J is used as the perturber it is 0.45 with $AgClO_4$. The concentration limit of perturber above which R_I becomes constant is ≈ 2 M for CH_3J and ≈ 0.75 M for $AgClO_4$. Also in pure CH_3J as a matrix R_I amounts to 1.5.

Apart from the different R_I values the phosphorescence spectra of triphenylene in the presence of CH_3J and $AgClO_4$ respectively are rather similar (Fig. 1, curves b and c).

However, the phosphorescence decay behaviour of triphenylene depends strongly on the type of perturber. As in many similar cases [3, 9] the decay curve is multi-exponential if CH_3J is used as the perturber, e.g. 4 time constants could be resolved at a CH_3J concentration of 1.8 M (0.6, 1.7, 4.2 and 15.6 sec the latter being the phosphorescence life-

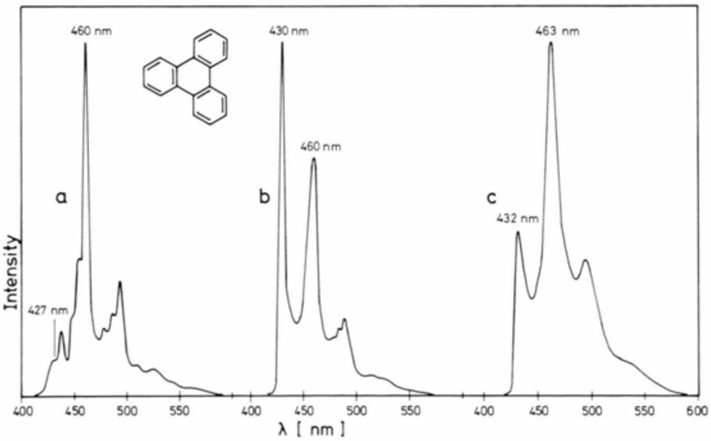

Fig. 1. Phosphorescence spectra of triphenylene ($2 \cdot 10^{-4}$ M) in ethanol at 77 K: a) in the absence of an external heavy-atom perturber, b) in the presence of methyl iodide (1.8 M), c) in the presence of silver perchlorate (1 M). (All spectra were normalized to the same heigth of the most intense band.)

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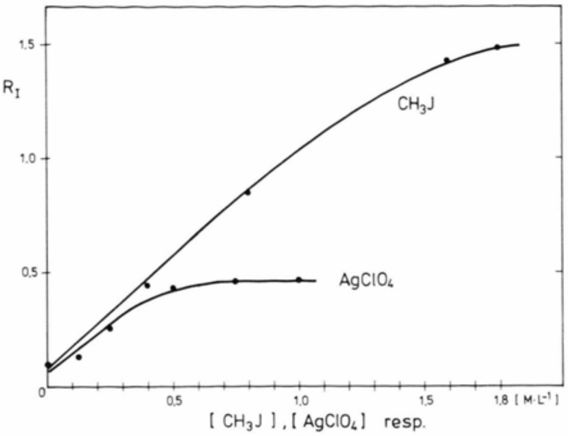

Fig. 2. Dependence of the ratio (R_I) of the intensities of the 0-0 band (427 nm) to the band at 460 nm of the triphenylene phosphorescence spectrum on the perturber concentration (CH_3J, $AgClO_4$) (Ethanol, 77 K).

time of the unperturbed molecule). On the contrary, the phosphorescence decay of triphenylene is monoexponential in the presence of $AgClO_4$ at a concentration $\geqq 0.75$ M (vide supra) exhibiting the phosphorescence lifetime (20 msec) of the triphenylene/$AgClO_4$ ground-state complex. Below this concentration the phosphorescence lifetime of the complex and the unperturbed triphenylene is observed. An analogous phosphorescence decay behaviour has been found in other aromatic donor molecule/silver salt systems [8]. It can be assumed that as in similar cases the Ag^+ ion induced increase of the rate constant k_{PT} of the radiative deactivation of the triphenylene triplet state is larger compared to the increase of k_{GT} of the radiationless deactivation [7].

For perturber molecules like methyl iodide for which associative forces between perturber and phosphorescent compound can be neglected, the exchange mechanism is well established as being responsible for the intensification of the 0-0 band in symmetry-forbidden phosphorescence transitions (vide supra, [4, 10]). Since the effect is purely electronic in nature, i.e. no vibronic coupling is involved, the extent to which spectral changes occur resembles that of changes in the phosphorescence lifetime. However, in the triphenylene/$AgClO_4$ system the change in phosphorescence lifetime is much larger compared to the triphenylene/CH_3J system but, on the other hand, the intensification of the 0-0 band is lower. Thus, another explanation for the spectral changes observed in the triphenylene/$AgClO_4$ system seems to be more likely.

The experimental results are consistent with the assumption that in the triphenylene/$AgClO_4$ system a phosphorescent ground-state complex is formed. In this complex the silver ion acts like a substituent which reduces the symmetry of the aromatic hydrocarbon and thus relaxes the symmetry-forbiddenness of the phosphorescence transition. Relaxation of the parity selection rule by substituents linked to centrally symmetric molecules whose phosphorescence transition is symmetry-forbidden is known in other cases, e.g. the very weak 0-0 band in the phosphorescence spectrum of coronene is significantly enhanced in the phosphorescence spectrum of methyl-coronene [11].

Experimental

The experiments were done on an Amino-Keirs spectrophosphorimeter using an oscillograph Tektronix 5403 for the phosphorescence lifetime measurements.

The triphenylene concentration used was always $2 \cdot 10^{-4}$ M.

The results obtained proved independent of the excitation wavelength.

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