The External Heavy Atom Effect on the Photodimerization of Thianaphthene 1,1-Dioxide

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Summary Bromoethane enhances the quantum yield of photodimerization of thianaphthene 1,1-dioxide by externally perturbing spin-orbital coupling and thereby enhancing intersystem crossing to the reactive triplet.

SPIN-ORBITAL perturbation of photoreactive molecules by heavy atoms is an area of considerable interest. The photochemistry of acenaphthylene has been the primary source of dramatic heavy-atom perturbation effects.[1,2] We report here that a different substrate, thianapthene 1,1-dioxide (TND), also fulfills the criteria[2] for an observable heavy-atom effect.

The molecule TND undergoes photodimerization at 313

$$\frac{1}{\phi_{DIM}} = \frac{1}{\alpha\phi_{ISC}} + \frac{1}{\alpha\phi_{ISC}}\left(\frac{k_d}{k_r}\right)\frac{1}{[TND]} \qquad (1)$$

nm in benzene solution and the reaction kinetics follow equation (1)[3] where ϕ_{DIM}, ϕ_{ISC}, α, k_d, and k_r are respectively the quantum yield of dimerization, the quantum yield of intersystem crossing $(S_1 \rightarrow T_1)$, the fraction of intermediates producing product, the excited triplet decay rate constant $(T_1 \rightarrow S_0)$, and the bimolecular rate constant for the addition of triplet state to ground state.

A plot of the data obtained by studying ϕ_{DIM} as a function of TND concentration in the solvent bromoethane gives a straight line from which ϕ_{ISC} is obtained because $\alpha = 1$[3] and the ratio k_d/k_r may be evaluated. The Table shows data from this study compared to prior data obtained in benzene solution.[3]

The intersystem crossing quantum yield for TND dramatically increases from 0·18 in benzene[3] to 1·0 in

bromoethane. Furthermore, the ratio k_d/k_r also increases when the solvent is changed from benzene to bromoethane. These changes can be explained as being caused by heavy-atom perturbation on both $S_1 \rightarrow T_1$ (ϕ_{ISC}) and $T_1 \rightarrow S_0$ (k_d).[2,4] The kinetic treatment implicitly verifies the heavy-atom effect on TND. The acceleration of the reaction in bromoethane is unrelated to its polarity because we have found that the photodimerization of TND in acetonitrile is considerably slower by a factor of about 10.

TABLE

Solvent dependence of photodimerization of TND

Solvent	ϕ_{ISC}	k_d/k_r /M	ϕ^{b}_{DIM}
Benzene[a]	0·18	0·22	0·017
Bromoethane	1·0	0·46	0·043
Acetonitrile	—	—	ca. 0·004

[a] Data calculated from ref. 3. [b] These values are for similar concentrations of TND of ca. 0·024 M.

The intermolecular heavy-atom effect is smaller for TND than for acenaphthylene. This may be the result of a smaller rate constant for internal conversion of excited singlet TND as compared to internal conversion in acenaphthylene excited singlet.[3] Because the TND system has proved a viable one for heavy-atom perturbation we anticipate that kinetic studies of the known photodimerization of brominated derivatives of TND[5,6] will be equally productive.

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