

Influence of restricted intramolecular motions on the fluorescence quantum yield

HANS GÜSTEN and ROLAND MEISNER

Kernforschungszentrum Karlsruhe, Institut für Radiochemie, 7500 Karlsruhe (F.R.G.)

Fluorescence spectra, fluorescence quantum yields and decay times were measured for aromatic molecules capable of either conformational or rotational mobility in dilute solutions of *n*-heptane and methylmethacrylate and in the rigid polymethylmethacrylate (PMMA) matrix at room temperature. On passing from fluid solutions to the polymeric matrix of PMMA a dramatic increase is obtained for the fluorescence quantum yield of *meso*-substituted anthracenes as well as structurally related molecules of stilbene and 1,3-diphenyl-2-pyrazoline. In some cases fluorescence spectra and quantum yields up to 0.5 can be measured in PMMA matrixes of compounds which do not fluoresce in solution. The rate constants for radiative and radiationless transitions in both media demonstrate that the increases in fluorescence quantum yields are exclusively due to the decreases in the rate constants for radiationless internal conversions. The rigidity of the PMMA matrix slows down the rates of intramolecular motions such as ring inversion or rotation of substituents and lengthens the time interval between excitation and achievement of those conformations that give rise to fast non-radiative decay. In solution these conformations are reached more rapidly and fluorescence is suppressed by the faster non-radiative deactivation of the excited singlet state.

Singlet charge transfer complexes between anthraquinones and electron donors

I. KAWENOKI, B. KEITA, J. KOSSANYI and L. NADJO

*Centre National de la Recherche Scientifique, Laboratoire de Photochimie Solaire,
2-8 rue H. Dunant, F-94320-Thiais (France)*

Singlet charge transfer complexes between variously substituted anthraquinones and electron donors (E_{ox}° from 0.35 to 1.76 V) were studied in acetonitrile solution by exciting the anthraquinones in their charge transfer absorption band. In each case a linear Stern-Volmer plot was obtained for the quenching of the fluorescence of the anthraquinone by the electron donor. The logarithm of the quenching rate constant, obtained after measurement of the singlet lifetime of the quinone by single-photon counting techniques, was observed to follow the Rehm and Weller equation. No emission of the electron donor-acceptor complex was observed in the present case, nor when ethanol was used as solvent. These results show that quinones behave as good electron acceptors from the singlet

state, as is already well known for their triplet state. The formation of the anthraquinone radical anion is discussed on the basis of the results obtained by flash photolysis.

Charge transfer quenching of $^3n,\pi^*$ and $^3\pi,\pi^*$ states by O_2 in the vapor phase

L. S. BUMGARNER, F. A. CEBUL, K. A. KIRK, D. W. LUPO, L. M. PITTENGER,
MERLYN D. SCHUH, M. P. THOMAS, I. R. WILLIAMS and G. C. WINSTON

Department of Chemistry, Davidson College, Davidson, NC 28036 (U.S.A.)

Flash-excited triplet state benzene was used to sensitize phosphorescence of 13 aldehydes and ketones by collision. The rate constant k_q for quenching of this phosphorescence by O_2 ranges between 0.056×10^9 and 6.9×10^9 $M^{-1} s^{-1}$.

The biacetyl sensitization method of Parmenter and Ring was used to determine the quenching of the triplet state of benzene and 12 benzene derivatives. k_q ranges between 1.2×10^9 and 1.2×10^{10} $M^{-1} s^{-1}$.

For all molecules a relationship exists between k_q and ionization potentials that supports a mechanism involving the formation of a triplet donor- O_2 complex coupled to a charge transfer state. The absence of a deuterium effect indicates the limited importance of Franck-Condon factors, which dominate in the quenching of $^3\pi,\pi^*$ state polycyclic aromatic hydrocarbons in solution.

The differences in quenching behavior of polycyclic aromatic hydrocarbons and benzene derivatives are discussed.

On the intramolecular decay and energy transfer in liquid alkanes

L. FLAMIGNI, F. BARIGELLETTI, S. DELLONTE and G. ORLANDI

*Istituto di Fotochimica e Radiazioni d'alta Energia del Consiglio Nazionale delle Ricerche,
Via de' Castagnoli 1, Bologna (Italy)*

Alkanes are known to have very low fluorescence quantum yields (10^{-3}) and lifetimes (10^{-9} s). To obtain information about the mechanism of deactivation paths after excitation in the singlet manifold, lifetime measurements were performed as a function of temperature. The excitation of alkanes was achieved by a two-photon absorption of a pulsed nitrogen laser beam. A further aspect investigated was the mechanism of energy transfer from a liquid alkane to a