PHOTOCHEMICAL REACTIONS OF ION PAIR COMPLEXES : QUANTUM YIELD DETERMINATIONS IN DIFFERENT MEDIA

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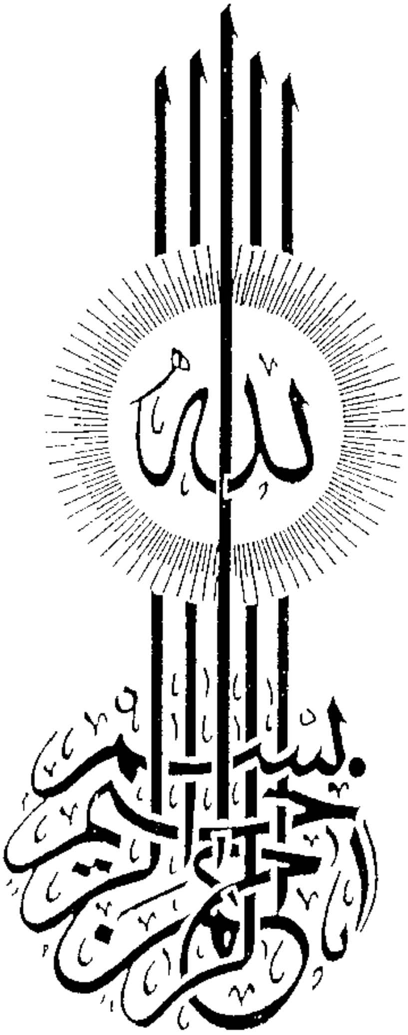
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TO MY PARENTS

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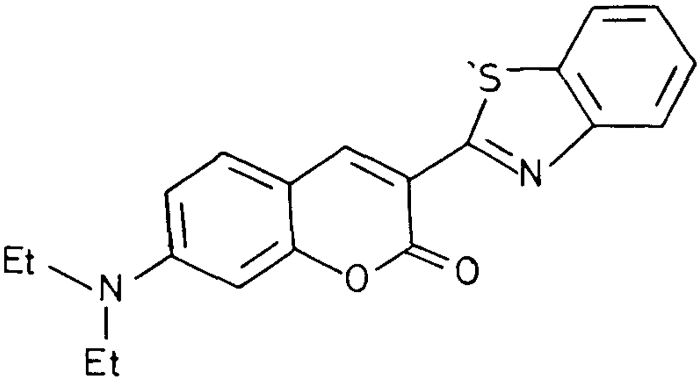
AIM OF THE WORK

Quenching processes of radiant energy have a significant bearing on structure requirements necessary to get essential information about some photochemical steps in a variety of solar energy conversion systems for increasing the efficiency of producing active quenchers.Also it provides molecular level information about excited state energy transfer which is routinely used in lasers and in molecular yardstick.

Since most coumarin derivatives in solutions have a strong fluorescence which depends on interactions with surroundings.they can be used as fluorescent probes for the investigation of various reactions among organic molecules .inorganic ions.and molecular aggregations

In the present work.the absorption and fluorescence spectra of aqueous and micellar solutions containing coumarin-6 (dye I) and 4-methyl-6-methoxy-8-t-butyl; coumarin (dye II)are measured precisely upon the addition of several inorganic fluorescence quenchers

We will report on the factors affecting the rate constant of fluorescence quenching of the above dyes by heavy atom effect induced by using iodine as a quencher and by electron transfer due to excited state interactions with some inorganic complexes of efficient redox ability like $[Fe(CN)_6]^{4-}$ (d^6-spin paired) and $[Fe(CN)_6]^{3-}$ (d^5-spin free)



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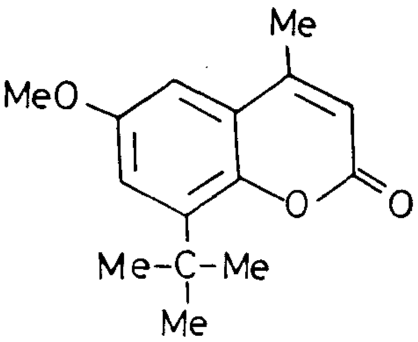

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RESULTS AND DISCUSSION *.

* Dye I = coumarin-6

Dye II = 4-methyl-6-methoxy-8-t-butyl-coumarin .

CHAPTER 1

GENERAL INTRODUTION

Chapter I

GENERAL INTRODUCTION

Electron transfer reaction have held a special place in chemistry because of their apparent simplicity . The progress in understanding these reactions in photosynthetic systems and the relevance of these processes to efficient utilization of solar energy have contributed to the momentum of advancement . In this study we restrict ourselves to a subtopic of this field that of fluorescence quenching due to excited state interactions of inorganic ions and complexes with some coumarin dyes .

The reactivity of an organic molecule in the first excited state is found to differ widely from that in its ground state . This difference can be due to the change in ionization potential, in charge distribution, and in geometry of the molecule upon excitation or to a combination of these factors . [1]

1-1- QUENCHING TERMINOLOGY . [2] .

According to Glossary, the

term quenching , which can be described as :

$$D^{*} + Q \longrightarrow \text{quenching} \longrightarrow \quad (1-1)$$

means the deactivation of an excited molecular entity by an external environmental influence (such as quencher) " . The definition of quencher, Q, is also based on the deactivation of excited donor molecules, D^{*} .

The term quenching covers both dynamic and static quenching which are defined as follows :

* When the external environmental influence (quencher) interferes with the behaviour of the excited state after its formation, the process is referred to as *dynamic quenching* .

* When the environmental influence inhibits the excited state formation, the process is referred to as *static quenching* . This definition of static quenching refers not only to the formation of DQ complex in the ground state which inhibits D^{*} molecules formation but also to the chemical reaction between D (in the ground state) and Q, and even the inner filter effect .

* In order to clarify the terminology and encourage its unambiguous use we would like to propose the following notions :

I. 1.1. QUENCHING :

Dynamic quenching should be understood as the process which depends upon diffusion of D^* and Q .

Static quenching should be referred to the case when Q is within the " sphere of action " of D^*, so that diffusion is not required for the quenching process .

I-1-2. *PSEUDOQUENCHING*

It refers to the case when a decrease in D^* concentration occurs as a consequence of a decrease in D concentration . So before D^* formation, e.g. as a result of DQ complex formation of D and Q in the ground states or even by the reactions between D and Q . The added substance Q will be then called a pseudoquencher .

I.1-3. INNER FILTER EFFECT

It is the case when the addition of Q does not decrease the concentration of D but diminishes the concentration of D^* as a consequence of competitive absorption of light .

The experimental criterion differentiating among quenching, pseudoquenching and inner filter effect could be the measurements of the excited state D^* lifetime . Quenching refers to the process which decrease the lifetime of D^*, whereas pseudoquenching and inner filter effect do not affect the excited state lifetime . All three processes, however, diminish the average concentration of D^* molecules, as determined, for example, by measuring a decrease in D^* emission intensity . The participation of inner filter effect, can be easily determined from absorption measurements It is obvious that in experimental practice we can deal with complex situations, when afore - described process may occur simultaneously .

I.2. KINETICS OF QUENCHING : STERN-VOLMER EQUATION . [3]

Under steady illumination, the rate of formation of an excited molecule D^* is equal to its rate of deactivation and the concentration $[D^*]$ remains constant :

$$\frac{d[D^*]}{dt} = 0 \longrightarrow (1-2)$$

The concentration of D^* in the absence of any bimolecular quenching step is given by

$$[D^*]^\circ = \frac{I_a}{k_f + k_{ic} + k_{isc}} = \frac{I_a}{k_f + \sum k_i} \longrightarrow (1-3)$$