the guenching effect of chloroform on electronic in some organic liquids

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GENERAL CONCLUSIONAlthough the mechanism of emrgy transfer for the quenching systems studied in this thesis are interpretted on the basis of virtual photon transfer, the results could also, but with more difficulty, be made compatible with the predictions of a real photon transfer.The quenching efficiency of chloroform for the systems studied in this work is greater than would be expected on the basis of a diffusion-limitted process with geometric cross-sections for solvent and quencher. This conclusion is based on comparison between theoritical calculationsand exp:rimental results for the specific rates K7 and K3. Since K1 is interpretted as the reciprocal of the lifeour results.chloroform system andK7 = -245.095 x 108 L/mole.sec. for naphthol + toluene + chloroform system, comparing it with the the oritical calculations according to equation oftime and as this value for toluene is 1.4 x 108 sec. (47) so we can now estimate the specific rates K7 and K3 forThese become respectively K7 = 424.15 x 108 L/mole.sec., K3 = 141.39 x 108 L/mole.sec, for anthracene + xylene +La Itier(47)K which gives a value for K7,3 equals to 142.88 x 108 L/mole.sec. It is clear that the specificrates K7 and K3 have values larger than would be expected of the energy quenching and energy transfer -reactions to be discussed as diffusion controlled with geometric cross sections,Arguments are also advanced against either of these reactions involving a long-range dipole-dipole interaction. It seemed that both the energy transfer and quenching processes somehow involved the intermediate participation of neighbouring solvent molecules. The diffusion of the excitation away from an initially excited toluene molecule via randomly oriented neighbouring toluene molecules to betoo slow because of the largestokes shift. It was there-fore postulated that a degree of short-range order excited in liquid toluene. The initial energy absorption act is assumed now to excite an excito.n state of the ordered region resulting in delocalization of the energy over the dimensions of the region. According to this view the rateThe equation of La K7,3 -r” 7.6 x 1021 where D is the sum two reactants, and reaction (R = 5 xMen.DR L/mole.sec.of the diffusion constants for the R is the intermolecular distanoe at 10-8 cmdetermining step in the energy transfer and quenching reactions would be the molecular diffusion of solute and quencher to the excited region. The specific rates K7and K3 should therefore be equal to the encounter frequency of the molecule with any point of this region.As a conclusion, our results are summerized as the occurance of both quenching by and energy transfer from chloroform. The solvent (toluene or xylene) acts as trapped medium of the energy from which it transported to both quencher (chloroform) and solute (anthracene or naphthol). Rapidly quenching of energy in chloroform occurs; a small fraction of this energy transferred tosolute via chloroform molecules.Increasing chloroform concentration results in more energy transference to it by the excited solvent molecule until the amount of energy transferred from chloroform to the solute (anthracene or naphthol) becomes significant compared to that transferred directly from solvent tosolute and this increases the self quenching of the system.Comparing the mathematical calculations of the pro-babilities of energy transfer (rate constant ratios), from solvent to solute (K3/K1) , and from solvent to quencher (K7/K1) we obtain that (K7/1(1) is greater than K3/K1 for the three systems and this means that chloroform acts asa good quencher. Also, by comparing the transfer parameter K3/Ki; firstly in case of naphthol + toluene + chloroform and anthracene + toluene + chloroform systems at the same conditions we obtain that KIKI for the first system is greater than that at the later one and this means thatthe transferred energy to naphthol is greater than in case of anthracene. Secondly•’ K3 /K1 in the case of anthracene + rylone + chloroform is greater than -K3/1(1 in the case of anthracene + toluene + chloroform systems at the same con ditions which means that the self quenching for the firstsystem is higher than that for the latter.When adding a high fluorescence solute as POPOP to a system, anthracene and naphthol in this case considered as intermediate solvents. The energy is transferred from both chloroform and intermediate solvent molecules to the solute (POPOP) molecules which is responsible for fluorescence emission. Results show that there is an increase in light output emission, i.e., the part of energy which is trans-ferred to the solute via intermediate solvent increases with increasing solute concentration. This means that the solute (POPOP) has overcome the quenching effect of thequencher chlorof orm .