

## Electronic Excitation Energy Quenching of PPD by CCl<sub>4</sub> in Different Solvents

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The electronic excitation energy quenching of 2, 5-Diphenyl-1, 3, 4-oxadiazole (PPD) by Carbon tetrachloride (CCl<sub>4</sub>) in different solvents viz, n-hexane, n-heptane, toluene, benzene, cyclohexane, 1, 4- dioxane has been carried out at room temperature to understand the role of quenching mechanism. The Stern-Volmer plots have been found to be linear. As probability of quenching per encounter 'p' is less than unity, and the activation energy for quenching 'E<sub>a</sub>' is greater than the activation energy of diffusion 'E<sub>d</sub>', it is inferred that the fluorescence quenching mechanism is not due to material diffusion alone.

**key words:** Oxadiazole, Fluorescence quenching, Stern-Volmer plot, Activation energy, Material diffusion.

### INTRODUCTION

Fluorescence quenching is a process, which decreases the fluorescence intensity of sample by a variety of molecular interactions such as excited-state reactions, molecular rearrangements, energy transfer, ground-state complex formation, collisional quenching etc. Fluorescence quenching of organic molecules in solution by various quenchers like carbon tetrachloride (CCl<sub>4</sub>), aniline, bromobenzene, halide ions etc., has been studied by several investigators [1-11]. This study has not only been of importance in physical sciences but also in chemical, biological and medical sciences [12-18]. In many cases the experimental results follow the linear Stern-Volmer (S-V) relation which is given by [19].

$$\frac{I_0}{I} = 1 + k_q \tau_0 [Q] \quad (1)$$

where I<sub>0</sub> and I are the fluorescence intensity in the absence and presence of the quencher at a concentration [Q] and k<sub>q</sub> is the quenching rate parameter. τ<sub>0</sub> is the fluorescence lifetime of the solute without quencher. The term k<sub>q</sub>τ<sub>0</sub> is called the Stern-Volmer constant K<sub>sv</sub>, which is obtained from the slope of Stern-Volmer plot.

The quenching phenomena can be understood due to short-range collision between the excited solute molecules and the quencher molecules [2-3]. If the close collision between the excited molecule and quencher molecule occur, the two reactants should occupy a contiguous position in the solution and separated due to diffusion after the collisional encounter. In solutions, the reactants before separating due to diffusion

undergo numerous mutual collisions of which each series represents an encounter. The probability of quenching per encounter is symbolically represented by 'p', which is less than unity, and the frequency of encounter is represented by k<sub>d</sub>. The quenching rate parameter k<sub>q</sub> is then given by

$$k_q = k_d p \quad (2)$$

The theoretical equation for the bimolecular reactions controlled by material diffusion is given by

$$k_d = \frac{4\pi NDR}{1000} \left\{ 1 + R(2D\tau_0)^{\frac{1}{2}} \right\} \quad (3)$$

where N is the Avogadro's number, D(=D<sub>Y</sub>+D<sub>Q</sub>) and R(=R<sub>Y</sub>+R<sub>Q</sub>) represents the sum of the diffusion coefficients and sum of the molecular radii of the solute and quencher respectively. The degree to which material diffusion controls the quenching and also efficiency of quenching can be determined by comparing the values of k<sub>d</sub> with k<sub>q</sub>. In the present work we have studied the steady state fluorescence quenching of 2, 5-Diphenyl- 1,3,4-oxadiazole (PPD) scintillator at room temperature using CCl<sub>4</sub> as quencher in different organic solvents namely n-hexane, n-heptane, toluene, benzene, cyclohexane, and 1,4- Dioxane.

### EXPERIMENTAL SECCION

The solute PPD was obtained from Sigma -Aldrich, USA, and is of scintillation grade and used as obtained. Its molecular structure is shown in Figure 1. The quencher CCl<sub>4</sub> was obtained from BDH Laboratory UK, and was of HPLC grade. The solvents were of HPLC grade and were used without further purification. The solutions were prepared

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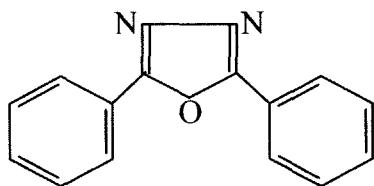


Fig. 1. Molecular structure of PPD.

keeping the concentration of PPD fixed (at  $1 \times 10^{-5}$  M/L) and varying the concentration of quencher (0.2-1.0 M/L). The solute was excited at 285 nm and the fluorescence spectrum was recorded. The fluorescence maximum corresponds to 345 nm. Fluorescence intensity of all the solutions was measured using Hitachi F-2000 spectrofluorimeter at room temperature. First the fluorescence intensity  $I_0$  was measured without the quencher and the fluorescence intensity  $I$  was measured at different quencher concentrations at a fixed solute concentration. The experimental values are reproducible within 5% of the experimental error. The details of experimental setup is discussed elsewhere[5].

## RESULTS AND DISCUSSION

The fluorescence intensities  $I_0$  and  $I$  were measured without and with quencher respectively at different quencher concentrations and at a fixed solute concentration. The typical emission spectra at different concentration of quencher  $\text{CCl}_4$  is shown in Fig. 2 for 1,4-dioxane solvent. The Stern-Volmer plots  $I_0/I$  versus  $[Q]$  in different solvents are shown in Figure 3 and they are found to be linear with intercept nearly equal to unity. This clearly shows that the phenomenon of quenching follows S-V relation. Using least square fit method the slopes  $k_q \tau_0 (= K_{sv})$  for steady state measurements using equation (1) were determined in each solvent medium. The quenching rate parameter  $k_q$  was determined for all the solvents by using the relation  $k_q = K_{sv}/\tau_0$ . The rate constant  $k_d$  of the bimolecular reactions, controlled purely by material diffusion, can be calculated according to the equation (3) using the numerical

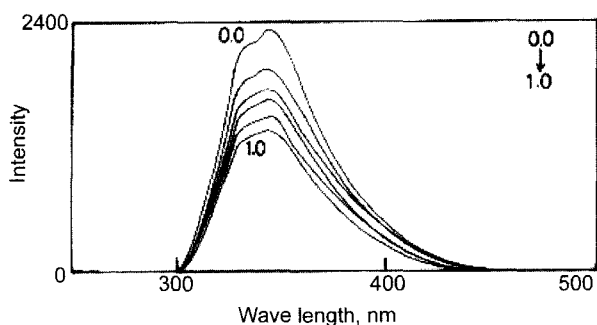


Fig. 2. Typical emission spectra of PPD at different quencher concentration of  $\text{CCl}_4$  [0.0 to 1.0 M/l].

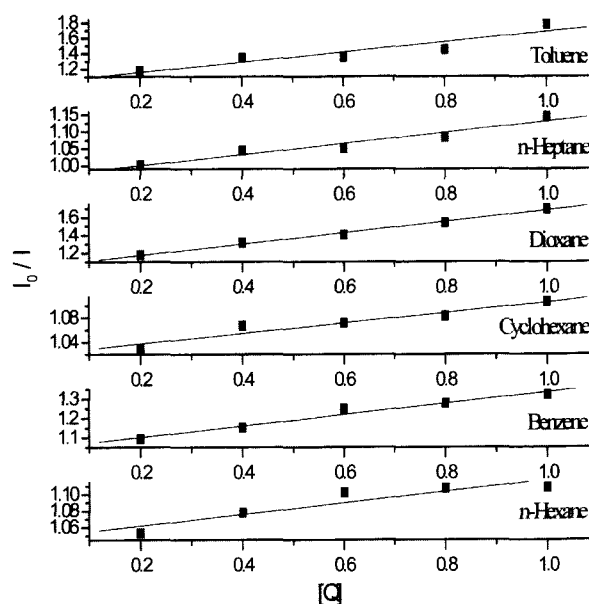


Fig. 3. Stern-Volmer plots of  $I_0/I$  against  $[Q]$  for PPD in different solvents.

values of the sum of the diffusion coefficients  $D (=D_Y + D_Q)$  and sum of the molecular radii  $R (=R_Y + R_Q)$  of the solute and the quencher respectively. The diffusion coefficient of solute  $D_Y$  and quencher  $D_Q$  can be calculated by using Stokes-Einstein equation

$$D = kT / a\eta R \quad (4)$$

where  $k$  is the Boltzmann's constant,  $\eta$  the absolute temperature,  $h$  the viscosity of the solvent,  $R$  the radius of the solute or quencher as the case may be, and ' $a$ ' the Stokes-Einstein number. In the present case, the radius of the solute molecule is larger than the solvent molecule, and that of the quencher molecule is close to the solvent molecule. Hence we have taken  $a = 3$  for quencher and  $a = 6$  for the solute [21]. Earlier work has been done from our group [22] on the experimental determination of diffusion coefficients of large number of solutes and quenchers in a number of solvents. From the study it has been found that the theoretical values of diffusion coefficients agree well with experimental values

Table 1. The values of inverse of viscosity  $\eta^{-1}$ , slope ( $k_q \tau_0$ ), quenching rate parameter  $k_q$ , and quenching probability per encounter  $p$ .

Solvent	$\eta^{-1} \times 10^{-2}$ $\text{p}^{-1}$	$k_q \tau_0$ $\text{m}^{-1}$	$k_q \times 10^{-9}$ $\text{m}^{-1}\text{s}^{-1}$	$p \times 10^3$
n-Hexane	3.35	0.07	0.06	1.68
n-Heptane	2.35	0.16	0.14	5.17
Toluene	1.81	0.63	0.54	27.00
Benzene	1.66	0.29	0.25	14.00
Cyclohexane	1.11	0.09	0.07	6.71
1,4,Dioxane	0.83	0.63	0.54	61.00

[  $\tau = 1.163$  ns.]

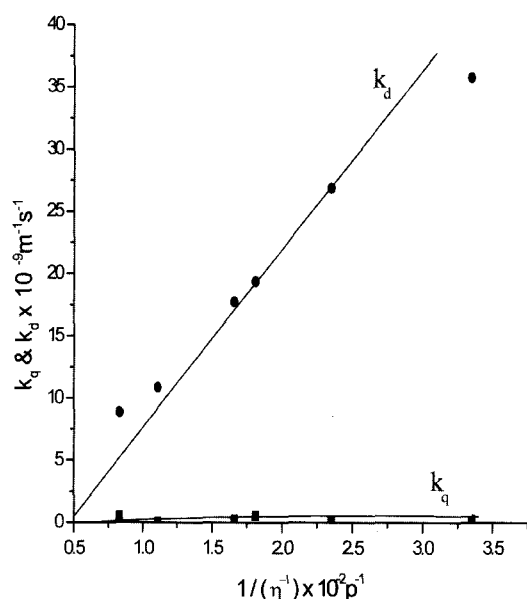


Fig. 4. Variation of  $k_q$  and  $k_d$  as a function of inverse of the viscosity  $h^{-1} \times 10^{-2} p^{-1}$  of the solvents.

when Stoke-Einstein number  $a$  is taken as 6 for diffusion of solute molecules of larger radius and  $a = 3$  for diffusion of quencher molecules of small or nearly equal radius as that of the radius of solvent molecules. The radius of the solute  $R_Y$  and the quencher  $R_Q$  have been calculated as suggested by Edward [20] and the values are given at the bottom of the Table 1.

Further, the probability of quenching per encounter has been determined experimentally according to equation (2) and the values are tabulated in Table 1. It is observed that the values of  $p$  are less than unity for all the solvents confirming that quenching is only due to collision between solute and quencher molecules. Therefore, the reactions of quenching are not solely controlled by material diffusion in which case  $p = 1$ .

Further, from Figure 4 it is observed that although the frequency of collisional encounter  $k_d$  increases with decrease in viscosity of the solvents, the quenching rate parameter  $k_q$  does not depend on the viscosity of the solvent. Hence it is inferred that the phenomenon of quenching is not solely controlled by material diffusion. If so, the values of  $k_q$  would have been equal to  $k_d$  and hence  $p$  is equal to unity in all the cases. Therefore in addition to diffusion it may also depend on the activation processes.

The activation energies for quenching reaction  $E_a$  in accordance with the equation

$$E_a = E_d + R T \ln[1/p - 1] \quad (5)$$

have been calculated using experimentally determined values of  $p$  along with the literature values of  $E_d$  and the gas constant  $R$ . The values are shown in the Table 2.

From these data it is observed that the activation energy ( $E_a$ ) for quenching is consistently larger than activation

Table 2. The Values of diffusion coefficients  $D_Y$  and  $D_Q$  of the solute and quencher respectively, diffusion rate parameter  $k_d$ , activation energy for diffusion  $E_d$ , and activation energy for quenching  $E_a$ .

Solvent	$D_Y \times 10^5$ $\text{cm}^2 \text{s}^{-1}$	$D_Q \times 10^5$ $\text{cm}^2 \text{s}^{-1}$	$k_d \times 10^{-9}$ $\text{m}^{-1} \text{s}^{-1}$	$E_d$ $\text{kcalmole}^{-1}$	$E_a$ $\text{kcalmole}^{-1}$
n-Hexane	2.01	5.39	35.80	2.07	18.01
n-Heptane	1.51	4.05	26.88	2.19	15.31
Toluene	1.09	2.91	19.38	2.66	17.75
Benzene	1.00	2.67	17.74	3.00	13.61
Cyclohexane	0.61	1.64	10.89	3.27	15.68
1,4,Dioxane	0.50	1.34	8.87	3.06	9.88

$$R_Y = 3.662 \text{ \AA} \quad R_Q = 2.733 \text{ \AA}$$

energy for diffusion ( $E_d$ ). This proves that the quenching reaction is not controlled by material diffusion alone and may also governed by activation process.

## CONCLUSION

From the ongoing discussion we found that 1) S-V plots are linear in all the solvents. 2) The value of probability per encounter  $p$  is less than unity in all the solvents. 3) The value of  $E_a$ , activation energy for quenching process is greater than  $E_d$ , activation energy for diffusion in all the solvents. In view of these results we may conclude that the quenching reaction of PPD by CCl<sub>4</sub> in different solvents is not solely controlled by material diffusion.

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