

FLUORESCENCE QUENCHING OF AMINODIPHENYLAMINES WITH CHLOROMETHANES

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The fluorescence quenching of 2-aminodiphenylamine (2ADPA), 4-aminodiphenylamine (4ADPA) and 4,4'-diaminodiphenylamine (DADPA) with tetrachloromethane, chloroform and dichloromethane have been studied in hexane, dioxane, acetonitrile and methanol as solvents. The quenching rate constants for the process have also been obtained by measuring the lifetimes of the fluorophores. The quenching was found to be dynamic in all cases. For 2ADPA and 4ADPA, the quenching rate constants of CCl₄ and CHCl₃ depend on the viscosity, whereas in the case of CH₂Cl₂, k_q depends on polarity. The quenching rate constants for DADPA with CCl₄ are viscosity-dependent but the quenching with CHCl₃ and CH₂Cl₂ depends on the polarity of the solvents. From the results, the quenching mechanism is explained by the formation of a non-emissive complex involving a charge-transfer interaction between the electronically excited fluorophores and ground-state chloromethanes.

Keywords: Fluorescence quenching; Dynamic quenching; Aminodiphenylamines; Non-emissive exciplex; Chloromethanes; Quenchers; Fluorescence spectroscopy; Solvent effects.

Haloalkanes have typically been investigated as quenchers of fluorescence of aromatic hydrocarbons and their derivatives¹⁻¹⁰. The observation of fluorescence quenching in such cases where there is negligible overlap of donor emission and acceptor absorption spectra was rationalized by Labianca *et al.*³ in terms of a non-emissive exciplex intermediate. Since direct observation of non-fluorescent exciplex is not possible, information about their formation can only be inferred^{11,12}. Klein *et al.*¹³ developed a model in which the formation of the charge transfer non-emissive exciplex was considered as the rate-determining step in excitation quenching process. The model predicts that the quenching rate constants (k_q) for a series of donors with an acceptor are related by the following expression:

$$\ln k_q \propto -(\text{IP}_D - \text{EA}_A - C - P - E_S)/kT, \quad (1)$$

where IP_D is the ionization potential of the donor, EA_A is the electron affinity of the acceptor, C is the Coulomb energy, k is the Boltzmann constant and P is the polarization energy of the separated charges, E_S represents the energy of the first excited singlet state of the fluorophore. Generally, with a common fluorescent donor and a series of different electron-deficient quenchers, the bimolecular rate constants can be correlated with the corresponding EA values of the quenchers. Other correlations have sometimes been made for different fluorophores and a single quencher but both IP_D and E_S values change simultaneously in the series of aromatics, which have been reported, so that k_q had to be correlated with $(IP_D - E_S)$. In our earlier study on the solvatochromic behavior of aminodiphenylamines¹⁴, we observed that the fluorescence intensities of aminodiphenylamines decrease so much in chloromethane solvents. Present work deals with the fluorescence quenching of 2-aminodiphenylamine, 4-aminodiphenylamine and 4,4'-diaminodiphenylamine with chloromethanes (CCl_4 , $CHCl_3$ and CH_2Cl_2) in non-polar and polar solvents such as hexane, dioxane, acetonitrile and methanol to investigate the mechanism of quenching in detail.

MATERIALS AND METHODS

2-Aminodiphenylamine, 4-aminodiphenylamine and 4,4'-diaminodiphenylamine, were obtained from Aldrich. The compounds were purified by recrystallization from suitable solvents. Spectrograde CH_2Cl_2 , $CHCl_3$, CCl_4 and other solvents were obtained from Merck and used as such. For all the quenching experiments, 10^{-4} M stock solutions of fluorophore were prepared. The quencher concentrations were varied using the respective stock solutions, so as to achieve desirable final concentration of quencher and fluorophores. Freshly prepared solutions were used for all experiments. CH_2Cl_2 being a very poor quencher, a high concentration (5 M) had to be used to get any meaningful quenching.

Absorption and fluorescence spectra were obtained using a Hitachi U-2001 Double Beam spectrophotometer and a JASCO FP-550 spectrofluorimeter, respectively. The excitation wavelengths chosen were the absorption maxima of the respective fluorophores. Measurements of lifetimes of the fluorophores were made by using a Picosecond spectrofluorimeter (Tsunami, Spectra Physics, U.S.A.) with the excitation source Ti-Sapphire Laser. The pulse width of the laser is lower than 2 ps.

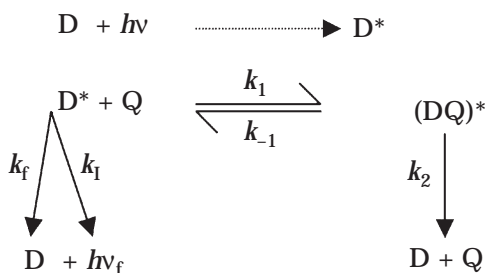
Cyclic voltammetric studies were made with potentiostat Wenking LB 75 M Model and voltage scan generator Wenking Model VSG-72 Model X-Y recorder. The three-electrode configurations are planar Beckman model

platinum inlay or glassy carbon as working electrode, a platinum flag sealed in soft glass as auxiliary electrode and saturated calomel electrode as reference electrode; they are uncorrected for function potentials. Tetrabutylammonium perchlorate (TBAP) was used as the supporting electrolyte. A sealed all-glass cell was used. Measurements were made under nitrogen atmosphere in acetonitrile as solvent at 298 K. The reference electrodes were separated from the experimental solution by a fitted bridge. This was filled with supporting electrolyte and the same solvent. Half-wave potentials were measured as the average of cathodic and anodic peak potentials.

RESULTS AND DISCUSSION

The following observations were made in absorption and fluorescence spectra of three compounds. (i) The shape and maxima of the longest-wavelength absorption band of the fluorophores do not change in the presence of any quencher in any solvent studied. (ii) The shape, maxima and frequency width at half maxima (FWHM) of the fluorescence spectra do not change in any solvent. (iii) The excitation spectra were very similar to their respective absorption spectra and (iv) no additional emission band was observed at longer wavelength indicating the absence of any new emissive species. The above observations seem to suggest that the fluorophore-quencher interaction does not change the absorption and fluorescence spectral properties. The absence of new fluorescence peak at longer wavelength reveals that there is no emissive exciplex formation. The quenching curves of all the fluorophores with three chloromethanes in hexane, dioxane, acetonitrile and methanol are linear. This shows that the quenching of three fluorophores with chloromethanes is dynamic in all the solvents. The Stern–Volmer constants K_{SV} for 2ADPA, 4ADPA and DADPA in all the four solvents have been obtained by the least-square fit method. The quenching rate constants (k_q) determined by using lifetimes of the fluorophores are given in Table I. The quenching constant decreases from CCl_4 to CH_2Cl_2 for all the three compounds. Tetrachloromethane is the best quencher. The k_q values of CCl_4 and CHCl_3 are nearly equal to k_{diff} values.

A popular mechanism, generally used to explain this kind of fluorescence quenching is as follows:



where D, Q and $h\nu$ represent the fluorophore, quencher and light quantum respectively, D^* and $(DQ)^*$ are the excited states of fluorophore and exciplex formed from the encounter complex, k_1 and k_{-1} are the rate constants, k_f and k_t are the rate constants for radiative and non-radiative monomer decay processes and k_2 is the decay rate constant of the excimer.

The apparent quenching rate constant for the above scheme can be written as $k_q = k_1\gamma$, where γ is the efficiency of the quenching reaction, which is given by $k_2/(k_2 + k_{-1})$.

Three different cases can arise in this mechanism:

(i) If $k_2 \gg k_{-1}$, then $k_{q(\text{obs})} \approx k_1 = k_{\text{diff}}$ (in the diffusion-controlled limit, which is a usual case of the excimer kinetics). As it is observed that the quenching process is dynamic in all cases, the fluorophore and quencher have to collide and thus the maximum value of k_q ($\approx k_1$) can be equal to the diffusion-controlled limits. The k_{diff} values ($\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$) for the solvents hexane ($3.42 \cdot 10^{10}$), acetonitrile ($2.87 \cdot 10^{10}$), methanol ($1.83 \cdot 10^{10}$) and dioxane ($0.847 \cdot 10^{10}$) have been taken from literature¹⁰. The value of k_q for fluorescence quenching of 2ADPA and 4ADPA with CCl_4 and CHCl_3 , and DADPA with CCl_4 are close to k_{diff} in all solvents. In these cases, the k_q values are viscosity-dependent. Thus the quenching efficiency is equal to unity, *i.e.*, every collision between D^* and Q leads to the deactivation and the rate is so high that hardly any back-diffusion is observed. Further, it is also known that a typical time requirement for equilibration of encounter complex leading to the exciplex formation is of the order 10^{-11} to 10^{-10} s. Since the rapid quenching is observed, it may be mentioned that the non-emissive exciplex (D^*Q) would not form completely and would be quenched before there is complete internal energy distribution and solvent cage reorientation.

(ii) If $k_2 \ll k_{-1}$, then $k_{q(\text{obs})} \approx (k_1/k_{-1})k_2 = Kk_2$, where, K is the equilibrium constant for the formation of exciplex. This implies that each collision does not lead to quenching and also that the quenching rate constant is independent of viscosity. On the other hand, if the exciplex formation involves

a charge transfer (CT) from the donor to the acceptor, the values of k_q are a function of the polarity of the solvent, *i.e.*, the CT complex is more stable in polar solvents and k_q increases with increase in polarity.

(iii) If $k_2 \cong k_{-1}$, k_q is lower than k_1 . So a clear dependence of k_q on solvent polarity or viscosity may not be observed.

The results (Table I) clearly indicate that the quenching of 2ADPA and 4ADPA fluorescence with CCl_4 and CHCl_3 and of DADPA fluorescence with CCl_4 correspond to case (i). The k_q values are high in hexane, the less viscous solvent and low in dioxane, the more viscous solvent. There is no correlation with the solvent polarity. This is due to the diffusion-limited quenching. For CH_2Cl_2 quenching of all the fluorophores and for CHCl_3 quenching of DADPA, the k_q values show a polarity dependence. The k_q values are high in more polar acetonitrile and low in less polar hexane. Furthermore, the quenching rates even in the case of CH_2Cl_2 are considerably faster than that can be accounted for by chemical quenching (for example, the rate constant of quenching of alkyl radicals with CCl_4 does not exceed $10^4\text{--}10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$)^{13,15}. Thus quenching must proceed *via* an intermediate donor-acceptor non-emissive exciplex between the excited fluorophore and chloromethane molecules. In order to verify this mechanism, the equation developed by Klein *et al.* for this model was used. With different quenchers for a constant fluorophore, Eq. (1) reduces to

$$\log k_q = \text{Const} + (\text{EA})/(2.303 kT) \quad (2)$$

and for different fluorophores and one quencher, Eq. (1) takes the form

$$\log k_q = \text{Const} + (E_s - \text{IP}_D)/(2.303 kT) . \quad (3)$$

The values of the ionization potentials were determined by cyclic voltammetry. Electron affinities were obtained from literature¹⁶. The singlet transition energy for the fluorophore was calculated by taking the average of the longest-wavelength-band maxima of the absorption spectrum and shortest-wavelength-band maxima of the fluorescence spectrum. The IP_D , E_s and EA values are given in Table II along with k_q values. The $\log k_q$ values of each fluorophore are plotted against electron affinity (EA) of the quenchers (Fig. 1) in a representative solvent acetonitrile. Although the number of quenchers is only three, it is clear from the figure that the quenching

increases with increase in EA. But the increase is not entirely linear. For each aminodiphenylamine the curves level off to a diffusion-controlled rate constant. A similar behavior has been reported in the fluorescence quenching of substituted naphthalenes¹⁰ and aromatic amines^{17,18}. The above results

TABLE II

EA of the quencher, IP_D , k_q , E_S , and ΔG values for aminodiphenylamine fluorescence quenching with chloromethanes in acetonitrile

| Fluorophore | IP_D , eV | E_S , eV | Quencher | $10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ | EA, eV | ΔG , eV |
|-------------|-------------|------------|--------------------------|---|--------|-----------------|
| 2ADPA | 0.950 | 3.83 | CCl_4 | 27.23 | 2.12 | -2.63 |
| | | | CHCl_3 | 17.03 | 1.75 | -1.43 |
| | | | CH_2Cl_2 | 0.080 | 1.36 | -0.74 |
| 4ADPA | 0.480 | 3.69 | CCl_4 | 15.47 | 2.12 | -2.96 |
| | | | CHCl_3 | 12.48 | 1.75 | -1.76 |
| | | | CH_2Cl_2 | 0.125 | 1.36 | -1.07 |
| DADPA | 0.700 | 3.66 | CCl_4 | 33.77 | 2.12 | -2.71 |
| | | | CHCl_3 | 18.23 | 1.75 | -1.51 |
| | | | CH_2Cl_2 | 0.105 | 1.36 | -0.82 |

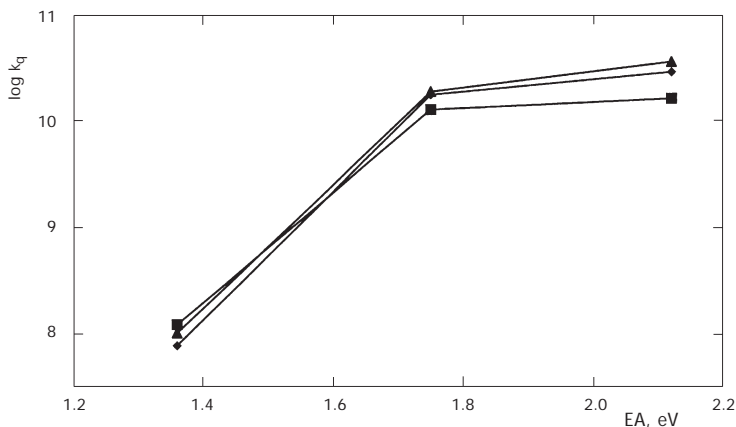


FIG. 1

Variation of $\log k_q$ against EA (eV) for aminodiphenylamines fluorescence quenching with chloromethanes in acetonitrile: ◆ 2ADPA, ■ 4ADPA, ▲ DADPA

are consistent with the fact that the values are limited by the electron affinity of the quencher as long as these values are lower than a diffusion-controlled limit. Once the value k_q is equal to k_{diff} , k_q is independent of EA.

The variation of $\log k_q$ with $(IP_D - E_S)$ in acetonitrile for all fluorophores with each quencher is shown in Fig. 2. Acetonitrile was chosen for this plot since IP_D values were determined only in acetonitrile. The linearity of the curves suggests a possible involvement of exciplex with charge transfer character, the charge being transferred from excited aminodiphenylamines to chloromethanes in the process of quenching. The plots for CCl_4 and $CHCl_3$ are nearly horizontal to x -axis. This again shows that once the value of k_q is equal to k_{diff} , k_q will be independent of $(IP_D - E_S)$.

This mechanism involving charge transfer can also be verified by the values of gibbs energy change (ΔG). When quenching occurs due to complex formation, the bimolecular quenching constant k_q can be related to ΔG ¹³ as

$$k_q \propto \exp(-\Delta G/RT) . \quad (4)$$

ΔG values for this charge transfer quenching process can be calculated using the equation¹⁷

$$\Delta G = E_{OX}(D/D^+) - E_{red}(A/A^-) - E_S - e^2/\epsilon r , \quad (5)$$

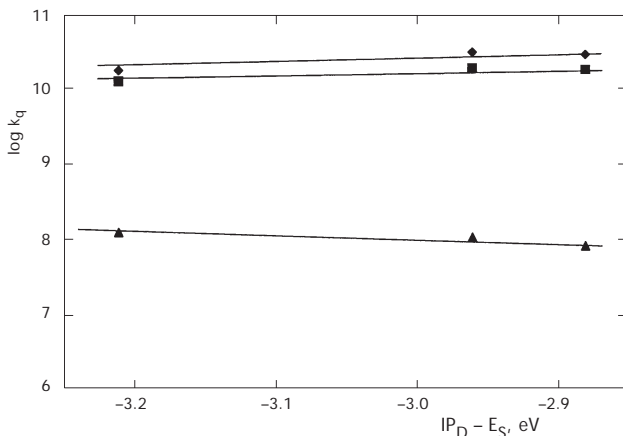


FIG. 2

Variation of $\log k_q$ against $(IP_D - E_S)$ for the fluorescence quenching of aminodiphenylamines with chloromethanes in acetonitrile: \blacklozenge CCl_4 , \blacksquare $CHCl_3$, \blacktriangle CH_2Cl_2

where E_{OX} (D/D^+) or IP_D and E_{red} (A/A^-) are the oxidation and reduction potentials of the donor (fluorophore) and acceptor (quencher), respectively, E_S is the singlet excitation energy of the fluorophore and $-e^2/\epsilon r$ is the Coulombic energy released upon transfer of an electron from D^* to A for the encounter distance r in a solvent with dielectric permittivity ϵ . The values of the reduction potentials of the CH_2Cl_2 , $CHCl_3$ and CCl_4 are taken from literature¹⁹ and these values are -2.24 eV (CH_2Cl_2), -1.55 eV ($CHCl_3$) and -0.35 eV (CCl_4). The Coulombic interaction has been taken as 0.1 eV in acetonitrile medium¹⁷. ΔG values have been calculated using the first oxidation potential of the fluorophores in acetonitrile medium and are given in Table II. The ΔG values are found to be negative. According to Eq. (4) the quenching rate constants increase as ΔG becomes more negative and reach a constant value k_{diff} for highly negative ΔG . For this mechanism to be operative, a linear correlation is expected between $\log k_q$ and ΔG values. This linear relationship occurs only when the k_q values are less than $10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. Since we have only three ΔG values for $k_q \leq 10^{10}$, we have taken the reported ΔG values of 2-aminodiphenyl and 4-aminodiphenyl²⁰ along with their k_q values. These ΔG values are plotted against $\log k_q$ values in Fig. 3. These two aminodiphenyls are found to follow the same quenching mechanism²⁰. For $k_q \leq 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, we have found a linear relationship

$$\log k_q = 6.14 - 2.27 \Delta G \quad (6)$$

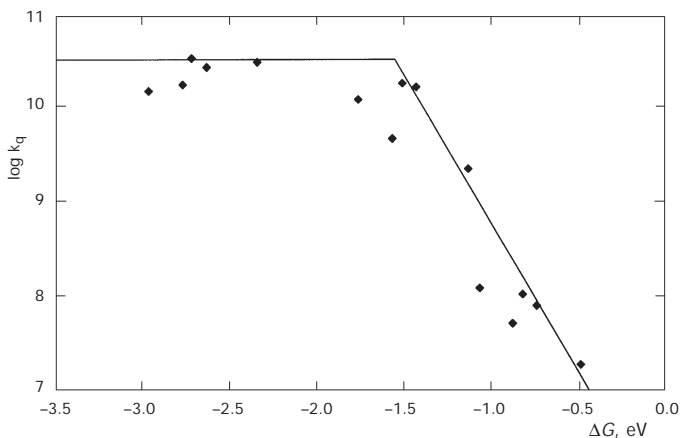


FIG. 3

Variation of $\log k_q$ against ΔG (eV) for the fluorescence quenching of aminodiphenylamines and aminodiphenyls with chloromethanes in acetonitrile

with the regression coefficient -0.91 . The linear portion of this plot supports the presence of CT in the exciplex formation in aminodiphenylamines.

The above results suggest that the fluorescence quenching for three aminodiphenylamines proceed *via* an intermediate donor-acceptor non-emissive charge-transfer complex formed between the excited aminodiphenylamine and quenchers.

CONCLUSION

On the basis of the above results it is concluded that (i) the fluorescence quenching is diffusion-controlled with the efficient quenchers CCl_4 and CHCl_3 (ii) the fluorescence quenching involves the formation of exciplex between donor and acceptor in the excited state showing charge-transfer character. Aminodiphenylamines serve as electron donors and chloromethanes as electron acceptors. (iii) No ground-state complex is formed between the fluorophore and quenchers.

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