Fluorescence Quenching of Some Isomeric Xylenols in Solutions

R. ROY & S. MUKHERJEE

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032

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Very dilute solutions of ethylenetrithiocarbonate (ETTC) is shown to quench the luminescence of 3,5-, 2,3-, 2,6- and 2,5-xylenols in cyclohexane when these solutions are excited with 280 nm light. These studies have been extended to dioxane, ethanol and acetonitrile solvents also. The effect of solvent on the rate constants of fluorescence quenching and quantum efficiencies of xylenols have been investigated for the non-emissive exciplex systems in which xylenols are the electron donors and ETTC an electron acceptor. The results suggest that a common mechanism is operating for all the systems and fluorescence is quenched primarily due to transfer of electronic excitation and charge transfer complex formation.

The non-radiative transfer of excitation energy of organic molecules has been discussed by many groups of workers\(^1\) -\(^3\). The process may be defined by the following two steps:

\[
D + h \rightarrow D^* \quad \text{(light absorption by donor)}
\]

\[
D^* + A \rightarrow D + A^* \quad \text{(energy transfer, donor \rightarrow acceptor)}
\]

Donor D* can transfer the electronic energy to a suitable acceptor molecule A resulting in quenching of D*. Fluorescence quenching has received wide attention\(^4\) -\(^9\). The present investigation on luminescence spectra of isomeric xylenol molecules (D) in polar and non-polar solvents at 300 K has been undertaken with a view to studying spectral changes in relation to charge transfer (CT) via H-bonding properties of these molecules in their electronically excited states and probable reaction processes leading to fluorescence quenching. The system most extensively characterized to date has been the dilute solution of fluorescer xylenol acting as an electron donor (D) and ethylenetrithiocarbonate (ETTC) as an electron acceptor (A), in solvents such as cyclohexane, dioxane, ethanol and acetonitrile.

Materials and Methods

The samples of isomeric xylenols (BDH and Fluka AG) were purified by recrystallization followed by sublimation. Cyclohexane (CH), dioxane (DO) and ethanol (ET) (all Merck, specpure) were dried over metallic sodium and distilled before use. ETTC (Fluka AG) was used as such. Acetonitrile (AN) (E Merck) was refluxed over KOH and fractionally distilled before use. Fluorescence studies were performed using a 1 cm quartz cell on a Perkin-Elmer M P F 44A fluorometer. Cyclohexane was used as an inert solvent in binary and ternary mixtures at 300 K. Blank runs were made with solvent alone, which did not show any fluorescence emission in the spectral region of interest. The electronic absorption spectra were run on a Cary 17D spectrophotometer.

Results and Discussion

At low concentrations the quenching of fluorescence by an acceptor molecule in solution follows the Stern-Volmer relation\(^10\) -\(^12\).

\[
\frac{I_0}{I} = 1 + K_Q [Q]
\]  \(\ldots (1)\)

where \(K_Q\) is the quenching constant, \(I_0\) is the steady state intensity of fluorescence at the quencher concentration \([Q]\) and \(I\) is its value without quencher. The Stern-Volmer equation predicts a linear dependence of \(I_0/I\) on \([Q]\) at least for most quenchers. By equating the bimolecular rate of quenching (constant \(K_q\)) against the rate of emission it can be easily shown\(^13\) that \(K_Q = K_r \tau\), where \(\tau\) is the actual mean life of the fluorescence, i.e. quantum efficiency \((\phi) \times \text{true radiative life} (\tau_0)\). The radiative life-time of xylenol molecules can be calculated from the familiar relation (2)

\[
\tau_N = \frac{1.5}{n^2(v_{max})^2 \times f}
\]  \(\ldots (2)\)

In Eq. (2), \(n\) is the refractive index of the medium, \(f\) is the oscillator strength and is given by \(f = 4.33 \times 10^{-9} \int \varepsilon d\lambda\). The quantum efficiencies \((\phi)\) are measured from the area under fluorescence curve relative to that of anthracene \((\phi = 0.32)\) under identical conditions\(^14\). The rate constant \((K_q)\) values are calculated from the diffusion formula \(K_d = 8RT/300\eta\), where \(\eta\) = liquid viscosity in poises.

When the solutions of xylenol molecules are excited with 280 nm light, emission spectrum in the region of

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Solvent effects

The quantum yield values given in Table 1 reveal almost linear correlation with the solvent polarity. Moreover, it is apparent that the increase in [ETTC] diminishes quantum yield values in polar as well as non-polar solvents for all the A-D pairs employed. On the other hand the $K_t$ values are higher in non-polar cyclohexane and dioxane but are lower in polar solvents such as ethanol and acetonitrile. Therefore, from the solvent polarity it is hard to perceive any solvent-induced changes in the mechanism of the fluorescence quenching, an observation which is inconsistent with the discussion based on dielectric formation, the fluorescence is strongly quenched. This was interpreted as due to π-interaction in the excited electronic state. Following this argument it may be presumed that the fluorescence quenching by ETTC, which has conjugate π-electron system, involves CT complexation with π-electron system of xylenol by the encounter collision in the excited state, immediately leading to non-radiative degradation of electronic excitation energy in xylenol. Moreover, ETTC quenches not only the fluorescence of xylenol but also the fluorescence of 2,5-dimethylanisole in different solvents, indicating that the quenching by ETTC is due to the molecular interaction other than H-bonding; probably the direct CT interaction. One point to note here is that the values of $K_Q$ and $K_t$ given in Table 1 are quite high. This may be due to the overlap between emission spectrum of donor (290-366 nm) and absorption spectrum of acceptor (260-340 nm). The greater the spectral overlap the more efficient is the energy transfer. Thus the rate constant ($K_t$) is independent of solvent viscosity and is greater than that ($K_d$) for diffusion-controlled reaction (Table 1).

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Table 1—Fluorescence Maxima (vF) and Excitation Maxima (vE), Fluorescence Efficiencies and Bimolecular Quenching Rate Constants of Some Xylenols by ETTC in Different Solvents at 300K

<table>
<thead>
<tr>
<th>Solvent</th>
<th>vF (cm(^{-1}))</th>
<th>vE (cm(^{-1}))</th>
<th>(\tau_\text{N} \times 10^8) (s)</th>
<th>(\phi_\text{p} (\phi_\text{p}))</th>
<th>(\tau(\text{ns}))</th>
<th>(K_\text{Q} \times 10^{-4}) (dm(^3) mol(^{-1}))</th>
<th>(K_\text{Kd}) (dm(^3) mol(^{-1}) s(^{-1}))</th>
<th>(K_\text{A}) (dm(^3) mol(^{-1}) s(^{-1}))</th>
<th>D.C.</th>
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<tr>
<td>CH</td>
<td>34282</td>
<td>35791</td>
<td>5.03</td>
<td>0.078 (0.069)</td>
<td>4.90</td>
<td>3.10 \times 10^{12}</td>
<td>6.48 \times 10^{9}</td>
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<td>ET</td>
<td>33333</td>
<td>35587</td>
<td>10.05</td>
<td>0.340 (0.350)</td>
<td>34.20</td>
<td>9.06 \times 10^{11}</td>
<td>6.65 \times 10^{9}</td>
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<tr>
<td>AN</td>
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<td>35587</td>
<td>8.07</td>
<td>0.371 (0.362)</td>
<td>29.94</td>
<td>13.69 \times 10^{11}</td>
<td>1.88 \times 10^{10}</td>
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<td></td>
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<td>35791</td>
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<td>0.052 (0.051)</td>
<td>2.41</td>
<td>3.58 \times 10^{12}</td>
<td>6.48 \times 10^{9}</td>
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<tr>
<td>ET</td>
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<td>35587</td>
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<td>13.96</td>
<td>20.76 \times 10^{11}</td>
<td>6.65 \times 10^{9}</td>
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<tr>
<td>ET</td>
<td>33557</td>
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<td>5.05</td>
<td>0.205 (0.182)</td>
<td>10.35</td>
<td>8.28 \times 10^{12}</td>
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<td>24.30</td>
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<td>4.98 \times 10^{12}</td>
<td>1.88 \times 10^{10}</td>
<td>37.20</td>
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<td>9.23 \times 10^{12}</td>
<td>—</td>
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</table>

Note: \(\phi_\text{p}\) = limiting quantum yields of photoreactions of different A-D pairs obtained from the usual plots of \(\phi_\text{p}^{-1}\) vs [A] \(^{-1}\) (in case where \(K_\text{Q}[A] < 1\) and \(\phi_\text{p}\) = quantum yields for disappearance of xylenols). D.C. = dielectric constant of solvent. All values of the quenching constants (\(K_\text{Q}\)) are derived from a least squares analysis of the linear Stern-Volmer plots. The values obtained are within ±10% of those obtained from the plots.

continuum. A probable reason could be that, since the donor molecules are polar solute of mobile \(\pi\)-electrons, the excitation energies may be perturbed by a variety of solute-solvent interactions including H-bonding in polar solvents.

References