Fluorescence quenching of substituted naphthalenes by inorganic anions

P K Behera
Department of Chemistry, Sambalpur University, Sambalpur 768 019 (India)

and

T Mukherjee
Chemistry Division, Bhabha Atomic Research Centre, Bombay 400 085 (India)

and

A K Mishra*
Department of Chemistry, I.I.T. Madras, Madras 600 036 (India)

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Quenching of fluorescence of six substituted naphthalenes by inorganic anions have been studied. The quenching is dynamic with the involvement of electron transfer from the anion to the fluorophore in the quenching process. The free energy ($\Delta G$) and the activation energy ($E_a$) of the electron transfer step has been estimated. Attempt is made to correlate the efficiency of quenching with these parameters.

Materials and Methods

1-Naphthol (1-ROH), 2-naphthol (2-ROH), 1-naphthylamine (1-RNH$_2$) and 2-naphthylamine (2-RNH$_2$) (Sisco Research Laboratories) were purified by repeated crystallisation from suitable solvents. 1-Methoxynaphthalene (1-ROMe) and 2-methoxynaphthalene (2-ROMe) were prepared in the laboratory from 1- and 2-ROH by using appropriate methods. The inorganic anions taken were the sodium salts of chloride (Cl$^-$), bromide (Br$^-$), iodide (I$^-$), sulphate (SO$_4^{2-}$), sulphite (SO$_3^{2-}$), thiosulphate (S$_2$O$_3^{2-}$), carbonate (CO$_3^{2-}$), nitrate (NO$_3^-$) and phosphate (HPO$_4^{2-}$) and were obtained from E. Merck, India.

Absorption and fluorescence spectra were obtained using a Hitachi-200 UV-vis spectrophotometer and Shimadzu RF-5000 spectrofluorimeter respectively. The excitation wavelengths chosen were the sodium salts of chloride (Cl$^-$), bromide (Br$^-$), iodide (I$^-$), sulphate (SO$_4^{2-}$), sulphite (SO$_3^{2-}$), thiosulphate (S$_2$O$_3^{2-}$), carbonate (CO$_3^{2-}$), nitrate (NO$_3^-$) and phosphate (HPO$_4^{2-}$) and were obtained from E. Merck, India.

Results and Discussion

The absorption and fluorescence spectra of all the fluorophores in the presence and absence of inorganic anions as quencher had the following characteristics, (i) the shape and maxima of the spectra did not change on addition of quenchers,
(ii) no new emission band was observed at the longer wavelength of the fluorescence spectra and
(iii) the excitation spectra in the presence of any inorganic anion closely resembled the excitation
and absorption spectra in the absence of inorganic anions. These results indicate that there is only
one emissive species and there is no emissive ex-
ciplex or ground state complex formed between
substituted naphthalenes and inorganic anions.
Sodium (Na\(^+\)) was chosen as the counter ion for
all inorganic anions because it has no effect on
quenching.

The Stern-Volmer plot of \(\frac{[I_0/I]-1}{[Q]}\) versus \([Q]\) is linear for all the fluorophores. The \(K_{SV}\) values
were calculated from the Stern-Volmer (SV) equation
\[
\frac{[I_0/I]-1}{[Q]} = K_{SV} \cdot [Q] = \left(\frac{k_q \cdot \tau_0}{k_d}\right) \cdot [Q] \quad \ldots \quad (1)
\]
where \(K_{SV}\) is the Stern-Volmer quenching constant, \(k_q\) is the bimolecular quenching constant and \(\tau_0\) is the fluorescence lifetime of the fluoro-
phore in the absence of quencher.

The \(k_q\) values obtained from the lifetime \(\tau_0\) for
all the fluorophores are given in Table 1. In
95% water, 1-ROH ionised completely in the ex-
cited state to give fluorescence of 1-naphtholate
(1-RO\(^-\)) whereas 2-ROH gives both neutral (2-
ROH) and anionic (2-RO\(^-\)) fluorescence. In the
case of 1-naphtholate (1-RO\(^-\)) and 2-naphtholate
(2-RO\(^-\)) ions there is negligible quenching due to
coulombic repulsion between fluorophore and
quenchers. From Table 1 it can be seen that quenching is maximum in the case of NO\(_3\)
and least in the case of SO\(_4^{2-}\). The \(k_q\) values obtained from all the cases are comparable with the \(k_d\)
value \((i.e. 10.61 \times 10^9 \text{ M}^{-1} \text{s}^{-1})\), which indicates
that the quenching is purely dynamic in nature\(^8\text{–}^{13}\).

From Table 1 it can also be seen that quenching in the case of amino substituted naphthalenes is
less compared to the other substituted naphtha-
lenes. One of the possible reasons may be a greater
excited state stabilisation of naphthylamines in
aqueous (polar) solvents as is reflected in larger
lifetime values and greater solvent shifts in the
emission spectrum. The greater degree of excited
state solvation may possibly inhibit quenching.

In earlier work, it has been suggested that, in
general, the quenching of aromatic hydrocarbons
by inorganic anions takes place via a transfer of
electrons\(^9\text{–}^{13}\). The electron transfer scheme can be
shown as\(^5\),

\[
\text{Products}
\]

\[
\text{1}^* \text{F} + 1^- \text{A} \xrightarrow{k_1} \text{1}^* \text{F}^- + 1^- \text{A} \quad \xrightarrow{k_2} 1^* \text{F}^- + 1^- \text{A} \quad \xrightarrow{k_3} \text{F}^- + 2^* \text{A}^- \quad \ldots \quad (2)
\]

From Scheme 1 it can be seen that there are
two rate determining steps in the bimolecular
quenching. First one is the translational diffusion
\((k_{diff})\) and the second one is the electron transfer
process \((k_2)\). Now, assuming electron transfer to
be exothermic \(k_{-2} \ll k_{diff}\) and the value of \(k_3\) to
be greater than \(k_{-2}\), Eq. (3) can be simplified as

\[
\frac{k_{diff}}{1+(k_{diff}/k_2)} \cdot [1+(k_{-2}/k_3)] \quad \ldots \quad (3)
\]

### Table 1—\(k_q\) and \(\tau_0\) of substituted naphthalene fluorescence by inorganic anions in 95% aqueous solution

<table>
<thead>
<tr>
<th>Fluorophore</th>
<th>Lifetime (ns)</th>
<th>(k_q \times 10^9) (M(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-ROH</td>
<td>4.84</td>
<td>Cl(^+), 0.28; Br(^-), 2.77; I(^-), 0.08; SO(_4^{2-}), 2.33; SO(_3^{2-}), 6.05; NO(_3), 3.51; S(_2)O(_4^{2-}), 1.53; CO(_3^{2-}), 2.02; HPO(_4^{2-}), 2.02</td>
</tr>
<tr>
<td>1-RNH(_2)</td>
<td>19.36</td>
<td>nq; 0.14; 0.47; 0.026; 0.13; 5.70; 1.99; 0.41; 0.066</td>
</tr>
<tr>
<td>2-RNH(_2)</td>
<td>16.75</td>
<td>nq; 0.11; 0.35; nq; 0.11; 3.33; 1.26; 0.03; 0.46</td>
</tr>
<tr>
<td>1-ROMe</td>
<td>10.38</td>
<td>nq; 0.5; 7.56; 0.22; 1.16; 9.06; 6.30; 0.59; 0.71</td>
</tr>
<tr>
<td>2-ROMe</td>
<td>9.41</td>
<td>nq; 0.2; 4.94; 0.15; 0.75; 7.07; 3.04; 0.18; 0.24</td>
</tr>
</tbody>
</table>

nq = No quenching.
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Table 2 – $k_q$, $E_{1/2}$, $E_s$, $E_{em}$, $EA$, $\Delta G$ and $E_s$ of substituted naphthalene-inorganic anion systems in 95% aqueous solution

<table>
<thead>
<tr>
<th>Fluorophore</th>
<th>$EA^*$ (eV)</th>
<th>$E_s$ (eV)</th>
<th>$E_{1/2}$ (eV)</th>
<th>$E_{em}$ (eV)</th>
<th>$k_q(M^{-1}s^{-1})$</th>
<th>$\Delta G_{TH}(eV)$</th>
<th>$E_s(eV)$</th>
<th>$\Delta G(eV)$</th>
<th>$E_{1/2}(eV)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-ROH</td>
<td>0.38</td>
<td>3.71</td>
<td>-2.60</td>
<td></td>
<td>2.77</td>
<td>-0.35</td>
<td>1.25</td>
<td>-0.38</td>
<td>-0.07</td>
</tr>
<tr>
<td>1-RNH$_2$</td>
<td>0.35</td>
<td>3.49</td>
<td></td>
<td></td>
<td>0.47</td>
<td>-3.08</td>
<td>-1.48</td>
<td>-3.34</td>
<td>-3.05</td>
</tr>
<tr>
<td>2-RNH$_2$</td>
<td>0.37</td>
<td>3.70</td>
<td>-2.60</td>
<td></td>
<td>0.35</td>
<td>-3.31</td>
<td>-1.71</td>
<td>-3.34</td>
<td>-3.03</td>
</tr>
<tr>
<td>1-ROMe</td>
<td>0.28</td>
<td>3.93</td>
<td>-2.60</td>
<td></td>
<td>0.94</td>
<td>-0.57</td>
<td>1.03</td>
<td>-0.6</td>
<td>-0.29</td>
</tr>
<tr>
<td>2-ROMe</td>
<td>0.37</td>
<td>3.90</td>
<td>-2.65</td>
<td></td>
<td>0.94</td>
<td>-3.45</td>
<td>-1.85</td>
<td>-3.48</td>
<td>-3.17</td>
</tr>
</tbody>
</table>

$*Electron affinity (EA)$ of the fluorophore obtained from the MNDO calculation.

$k_q = (k_2 + k_{\text{diff}})/(k_2 + k_{-\text{diff}})$

The free energy change $\Delta G$ in the electron transfer process can be calculated from Treinin and Hayon equation

$$\Delta G_{TH} = E_{\text{cts}} - E_{1/2} - E_s - 4.7$$

where $E_{\text{cts}}$ is the charge transfer to solvent transition energy of the inorganic quenchers, $E_{1/2}$ is the redox potential and $E_s$ is the singlet transition state energy for the fluorophores. All the units are in electron volt (eV). $E_{1/2}$ for the naphthylamines could not be determined because the reduction potential for these molecules are less than -2.5 V (ref. 6). Since the value of $E_{1/2}$ of the amines are not known, the electron affinity ($EA$) of the fluorophores as computed by using MNDO MO calculations were substituted for $E_{1/2}$ and the corresponding ($\Delta G$) is calculated. Linear correlation is known to exist between experimental $E_{1/2}$ and $EA$ calculated using HMO methods for certain classes of organic compounds.

$$\Delta G = E_{\text{cts}} - EA - E_s - 4.7$$

The data for inorganic anions for which $E_{\text{cts}}$ was available are listed in Table 2. A first order regression fit between $\Delta G$ and $\log k_q$ of each fluorophore gives the slopes as -1.04, -0.79, -0.75, -0.62 and -0.30 for 2-ROH, 2-ROMe, 1-ROMe, 1-RNH$_2$ and 2-RNH$_2$ which are in the order 2-ROH < 2-ROMe < 1-ROMe < 1-RNH$_2$ < 2-RNH$_2$ respectively. Thus for naphthylamines, not only the efficiency of quenching is the least, the slopes are also the least steep. The decrease in the magnitude of the slope has often been attributed to the formation of an intermediate donor-acceptor complex in the excited state resulting from incomplete charge transfer. Extending the analogy it can possibly be said that the greater excited state stabilisation of RNH$_2$ in the aqueous solvent results in a decreased efficiency of electron transfer in the excited state donor-acceptor complex.

With the available data we have calculated $\Delta G_{TH}$ for three fluorophores (2-ROH, 1-ROMe and 2-ROMe) and six inorganic anions (Cl$^-$, Br$^-$, I$^-$, SO$_3^-$, S$_2$O$^-$ and SO$_4^{2-}$ anions). The value of free energy change ($\Delta G_{TH}$) along with singlet transition energy ($E_s$), reduction potential ($E_{1/2}$) of fluorophore and $E_{em}$ energy of inorganic anions are given in the Table 2. From Table 2 it can be seen that $k_q$, in general, is more when reduction potential of fluorophore is higher and decreases with increase in $E_{em}$ energy of inorganic anions. A first order regression fit was attempted between $\Delta G_{TH}$ and $\log k_q$ of each fluorophores.
The slope and intercept calculated from the regression fit are $-0.85$ and $9.05$ respectively with a regression value ($r=0.98$). Thus we can write an equation of type

$$\log k_q = -0.85 \Delta G_{TH} + 9.05 \quad \ldots (7)$$

the linearity strongly suggesting the electron transfer nature of the quenching of substituted naphthalenes by inorganic anions.

Considering electron transfer to be the rate determining step in the quenching, we have $k_{-\text{diff}} > k_2$ and Eq. (4) can be written as,

$$k_q = \frac{k_2 \cdot k_{\text{diff}}}{k_{-\text{diff}}} \quad \ldots (8)$$

and the values of $k_2$ can be expressed by the Arrhenius equation as,

$$k_2 = A \exp(-E_a/RT) \quad \ldots (9)$$

where $A$ is the collisional frequency at unit molar concentration of reactants within the encounter complex and $E_a$ is the potential barrier in the electron transfer process. Substituting Eq. (9) in (8) we can write

$$k_q = \left[\frac{k_{\text{diff}} \cdot A}{k_{-\text{diff}}}\right] \exp\left(-\frac{E_a}{RT}\right) \quad \ldots (10)$$

Once more assuming $k_{\text{diff}} = k_{-\text{diff}}$, Eq. (10) becomes,

$$k_q = A \exp\left(-\frac{E_a}{RT}\right) \quad \ldots (11)$$

Taking the frequency factor $A$ to be $10^{10}$ as suggested by Shizuka et al., Eq. (11) can be written as,

$$k_q = 10^{10} \exp\left(-\frac{E_a}{RT}\right) \quad \ldots (12)$$

From Eqs (7) and (12) and at room temperature, an expression similar to the Polanyi rule formulation\textsuperscript{19} can be derived,

$$E_{a_{TH}} = 0.022 \Delta G_{TH} + 0.025 \quad \ldots (13)$$

This corresponds to the understanding that $\Delta(E_{a_{TH}})$ is proportional to $\Delta(\Delta G)$. $\Delta G_{TH}$ for the fluorophores calculated using the above equation, are given in Table 2. From Eq. (13), the value of $E_{a_{TH}}$ (activation energy when $\Delta G_{TH}$ is zero) comes to 0.025 which is comparable to those derived for similar systems\textsuperscript{5}. Equation (13) also suggests that at a $\Delta G_{TH}$ value of around $-1.136$ eV, the quenching process will be almost completely barrierless and purely diffusion controlled.

Acknowledgement

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