Photophysical and Photochemical Studies of Polycyclic Aromatic Hydrocarbons in Solutions containing Tetrachloromethane.

I. Fluorescence Quenching of Anthracene by Tetrachloromethane and its Complexes with Benzene, p-Xylene and Mesitylene

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Fluorescence quenching of anthracene has been studied in two-component mixtures of CC14 with cyclohexane, benzene, p-xylene and mesitylene. Non-typical quenching curves have been found in mixtures containing benzene and its derivatives.

1. Introduction

Chloromethane have been found to quench the fluorescence of aromatic hydrocarbons in solution [1–14]. The quenching in these systems is usually accompanied by chemical transformations resulting in the generation of free radicals [15–19]. Two mechanisms of the fluorescence quenching by CC14 have been envisaged:

(i) Transfer of the electronic excitation energy of the hydrocarbon to vibrations of the CC14 molecule.

(ii) Formation of a labile CT complex between the hydrocarbon in its S1 state and the quencher molecule.

There is ample evidence for the preponderance of the latter mechanism involving “external electron transfer”.

Tetrachloromethane has been found to form CT complexes with benzene and its methyl derivatives [20–23]. Hence, in two-component mixtures of CC14 with benzene or its derivatives, complexes of the former with the solvent molecules are likely to occur together with non-bonded (free) CC14 molecules. Fluorescence quenching of anthracene in such mixtures should thus be dependent on the concentration of both the non-bonded and bonded CC14 molecules. Consequently, different quenching efficiencies in either of the two forms of the CC14 molecules might be expected.

2. Experimental

Spectroscopically pure anthracene, benzene and cyclohexane were used as supplied for fluorescence experiments. A spectrograde tetrachloromethane was additionally purified by a procedure reported in [24]. p-xylene and mesitylene (sym-trimethylbenzene) were purified by refluxing over sodium metal for 5 h followed by fractional distillation.

Luminescence spectra were measured on a modular spectrofluorimeter according to Jasny [25], absorption spectra usually on a C. Zeiss Specord UV-VIS spectrophotometer.

Quantum yields were measured relative to quinine sulphate as a standard, Φ = 0.51 [26]. They were corrected for variations in the refractive index and absorbance readings due to the varied composition of the solutions as well as under consideration of the reabsorption. A mercury 366 nm line was used for excitation.

Fluorescence decay curves were measured by a sampling technique with an ns N2-laser excitation at the Institute of Physical Chemistry, Polish Academy of Sciences.

Fluorescence lifetimes were determined using a plane-phase method [27].

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3. Results and Discussion

Fluorescence quenching of aromatic hydrocarbons by chloromethanes in various media is reported in the literature for quencher concentrations not exceeding 1 M. In Fig. 1, fluorescence quenching curves are shown for anthracene over the entire accessible CC14 concentration region for non-deoxygenated solutions of the hydrocarbon in mixtures of CC14 with benzene [1], p-xylene [2], mesitylene [3] and cyclohexane [4].

The Stern-Volmer equation [7, 8] can only be applied to the CC14-cyclohexane mixture. The remaining mixtures display a maximum and obey the Stern-Volmer equation over a narrow concentration range of tetrachloromethane only, both in deoxygenated and non-deoxygenated solutions.

The addition of benzene, p-xylene or mesitylene to the cyclohexane solution of anthracene enhances only slightly the fluorescence intensity of the hydrocarbon while the presence of these components in a CC14-cyclohexane mixture of fixed composition reduces the fluorescence intensity remarkably (Figure 2). The efficiency of fluorescence quenching by CC14 is directly related to the benzene concentration.

The distinct increase in the fluorescence intensity caused by benzene or its derivatives can be interpreted as an additional quenching by CC14 complexes with benzene, p-xylene and mesitylene, which turned out to quench the fluorescence of anthracene more effectively than pure CC14.

The mixtures of CC14 with aromatic hydrocarbons were investigated by a variety of techniques. UV-spectrophotometric absorption measurements revealed new bands which were missing in the spectra of the pure components. The bands were ascribed by Prausnitz and associates [20, 21] to the formation of 1:1 CT complexes in which the hydrocarbons occurred as electron donors. The complex formation constants (M⁻¹) determined by Rosseinsky and Kellawi [22] at 25 °C are:

- benzene: 0.076 ± 0.057
- m-xylene: 0.112 ± 0.028
- p-xylene: 0.136 ± 0.018
- mesitylene: 0.252 ± 0.036
- hexamethylbenzene: 0.550 ± 0.160

The non-typical shape of the fluorescence quenching curves can be explained assuming two quenching species, a CC14 complex with the other component of the mixture and non-bonded CC14.

Assuming that the fluorescence quenching of anthracene by CC14 in p-xylene and mesitylene is dynamic in nature, as it is the case with cyclohexane and benzene (identical shapes of the relations \( \Phi_0/\Phi \) and \( \tau_0/\tau \); Figs. 3 and 4) [8] and utilizing the aforementioned formation constants [22], the fluorescence quenching curves for anthracene in the CC14 mixtures with benzene, p-xylene and mesitylene can be presented as an over-all affect of the fluorescence.
Fig. 3. Fluorescence lifetime of anthracene [1] (c = 1.6 x 10^{-4} M) and the magnitudes of $\Phi_0/\Phi$ (- - - ) and $\tau_{0}/\tau$ (---) [2] as functions of CCl$_4$ concentrations in the mixtures with cyclohexane.

Fig. 4. Fluorescence lifetime of anthracene [1] (c = 1.6 x 10^{-4} M) and the magnitudes of $\Phi_0/\Phi$ (- - - ) and $\tau_{0}/\tau$ (---) [2] as functions of CCl$_4$ concentrations in the mixtures with benzene.

Fig. 5. Relationship between the $\Phi_0/\Phi$ ratio of the fluorescence of anthracene (c = 1.6 x 10^{-4} M) in benzene and the CCl$_4$ concentration [1], CCl$_4$ non-bonded into a complex with benzene [2] and concentration of the C$_6$H$_6$·CCl$_4$ complex [3].

quenching of the hydrocarbon by both non-bonded and bonded tetrachloromethane.

By utilizing the ratio of the quantum yields of fluorescence of anthracene, $\Phi_0/\Phi$, determined in pure CCl$_4$ relative to benzene or its derivatives and assuming dynamic quenching, the Stern-Volmer constant

$$K_{SV} = \frac{\Phi/\Phi_0 - 1}{10.29}$$

can be estimated and yields the contribution of non-bonded CCl$_4$ to the experimental quenching curve:

$$(\Phi_0/\Phi)' = 1 + K_{SV}[\text{CCl}_4]_e,$$

where [CCl$_4$]$_e$ is the equilibrium concentration of non-bonded CCl$_4$ calculated on the basis of the formation constants and the initial concentrations of the components of the mixture. The difference between experimental quenching curve, $\Phi_0/\Phi$, and the quenching by non-bonded CCl$_4$, $\Phi_0/\Phi'$, gives the contribution of the C$_6$H$_6$·(CH$_3$)$_x$·CCl$_4$ ($x = 0, 2, 3$) complex to the fluorescence quenching of anthracene, $\Phi_0/\Phi''$ (Figure 5). In Fig. 6, $\Phi_0/\Phi''$ is
Medium Non-bonded CCl₄ C₆H₆-x/CH₃-x • CCl₄

<table>
<thead>
<tr>
<th>Medium</th>
<th>Non-bonded CCl₄</th>
<th>C₆H₆-x/CH₃-x • CCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>0.91 ± 0.01</td>
<td>0.224</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.01 ± 0.01</td>
<td>0.269</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>0.95 ± 0.01</td>
<td>0.279</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>0.84 ± 0.01</td>
<td>0.261</td>
</tr>
</tbody>
</table>

\( K_{SV} \) (M⁻¹) \( k' \times 10^{-9} \) (M⁻¹ s⁻¹) \( k'' \times 10^{-9} \) (M⁻¹ s⁻¹)

Table 1. The Stern-Volmer constants and the rate constants of the fluorescence quenching of anthracene by the non-bonded and bonded CCl₄ in various solvents.

The solutions were not deaerated prior to measurements.

Calculated by assuming the fluorescence lifetime \( \tau_0 \) as for benzene.

![Fig. 6. Fluorescence quenching of anthracene by the C₆H₆-x/CH₃-x • CCl₄ (x = 0, 2, 3) complexes.](image)
ISC in anthracene. Numerical values assumed in the calculations were \( k_q = 2.28 \times 10^8 \text{ m}^{-1} \text{s}^{-1} \) for cyclohexane, and \( k_q' = 2.01 \times 10^8 \text{ m}^{-1} \text{s}^{-1} \) and \( k_q'^2 = 1.95 \times 10^9 \text{ m}^{-1} \text{s}^{-1} \) for benzene.

The observed parabolic fluorescence quenching of anthracene is thus due to a specific interaction occurring in the solvent mixtures.

These pathways enable to suggest the following kinetic scheme of the photophysical and photochemical processes occurring in the systems under consideration:

\[
\begin{align*}
S + Q & \xrightarrow{K_1} SQ \xrightarrow{k_4/k_{-4}} (SQA)^* \xrightarrow{k_5} \text{products, A, Q, S} \\
A + Q & \xrightarrow{k_{11}} A + Q \xrightarrow{k_{10}} A* + Q \xrightarrow{k_{10}'} (A \cdots Q)^* \xrightarrow{k_5} \text{products, A, Q, S} \\
A + h v_f & \xrightarrow{3A} A + Q \xrightarrow{k_{12}} A Q + Q \rightleftharpoons A Q_2 + \ldots,
\end{align*}
\]

where A is the hydrocarbon, Q the quencher and S the solvent. For this scheme, the \( \Phi_0/\Phi \) ratio is determined by the equation

\[
\frac{\Phi_0}{\Phi} = \frac{1 + k_1 [Q] \tau_0 p + k_4 [SQ] \tau_0 p'}{1 - p x},
\]

where \( \tau_0 = (k_4 + k_{10} + k_{10}')^{-1} \) is the fluorescence lifetime of the hydrocarbon in the absence of quencher, \( p = k_3(k_5 + k_{-4})^{-1} \) and \( p' = k_5(k_5 + k_{-4})^{-1} \) determine the extent of the reaction of particular exciplexes, \( x \) determines the fraction of the exciting radiation absorbed by the AQ complex,

\[
x^{-1} = 1 + \left( \frac{\varepsilon_A}{\varepsilon_{AQ}} \right) \left( \frac{1}{K_2 [Q]_e} \right),
\]

and \([SQ]_e\) is the concentration of the complex of quencher with solvent.

In the case of formation by the quencher of a more efficiently quenching complex with a component of the mixture, the shape of the fluorescence quenching curve is parabolic owing to the nature of the relationship between the concentration of the complex being formed and the CCl\(_4\) concentration in the particular two-component mixture.

The processes of the fluorescence quenching of other hydrocarbons in CCl\(_4\) mixtures with solvents capable of forming sufficiently stable complexes with CCl\(_4\) are likely to resemble that of anthracene. Consequently, the shape of the fluorescence quenching curve can provide an indicator of intermolecular interactions. Oxygen present in the solutions does not induce qualitative changes in the systems under consideration in spite of causing additional reduction of the fluorescence intensity of anthracene [1, 28, 29].

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