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 CCl_4 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 CCl_4 have been envisaged:

(i) Transfer of the electronic excitation energy of the hydrocarbon to vibrations of the CCl_4 molecule.

(ii) Formation of a labile CT complex between the hydrocarbon in its S_1 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 CCl_4 with benzene or its derivatives, complexes of the former with the solvent molecules are likely to occur together with non-bonded (free) CCl_4 molecules. Fluorescence quenching of anthracene in such mixtures should thus be dependent on the concentration of both the non-bonded and bonded CCl_4 molecules. Consequently, different quenching efficiencies in either of the two forms of the CCl_4 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, $\Phi = 0.51$ [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 N_2-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 CCl_4 concentration region for non-deoxygenated solutions of the hydrocarbon in mixtures of CCl_4 with benzene [1], p-xylene [2], mesitylene [3] and cyclohexane [4].

The Stern-Volmer equation [7, 8] can only be applied to the CCl_4-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 CCl_4-cyclohexane mixture of fixed composition reduces the fluorescence intensity remarkably (Figure 2). The efficiency of fluorescence quenching by CCl_4 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 CCl_4 complexes with benzene, p-xylene and mesitylene, which turned out to quench the fluorescence of anthracene more effectively than pure CCl_4.

The mixtures of CCl_4 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 CCl_4 complex with the other component of the mixture and non-bonded CCl_4.

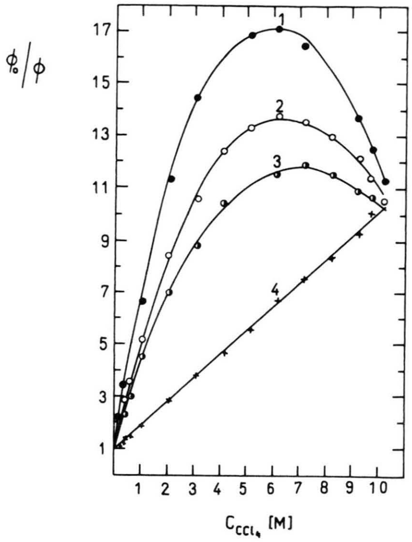


Fig. 1. Fluorescence quenching curves of anthracene ($c = 1.6 \times 10^{-4}$ M) by CCl_4 in benzene [1], p-xylene [2], mesitylene [3] and cyclohexane [4].

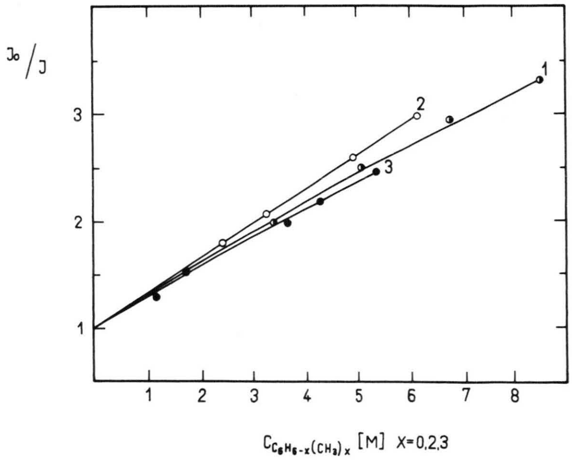


Fig. 2. Fluorescence quenching of anthracene ($c = 1.6 \times 10^{-4}$ M) by benzene [1], p-xylene [2] and mesitylene [3] in a 2.06 M cyclohexane solution of CCl_4.

Assuming that the fluorescence quenching of anthracene by CCl_4 in p-xylene and mesitylene is dynamic in nature, as it is the case with cyclohexane and benzene (identical shapes of the relations Φ_0/Φ and τ_0/τ; Figs. 3 and 4) [8] and utilizing the aforementioned formation constants [22], the fluorescence quenching curves for anthracene in the CCl_4 mixtures with benzene, p-xylene and mesitylene can be presented as an over-all affect of the fluorescence

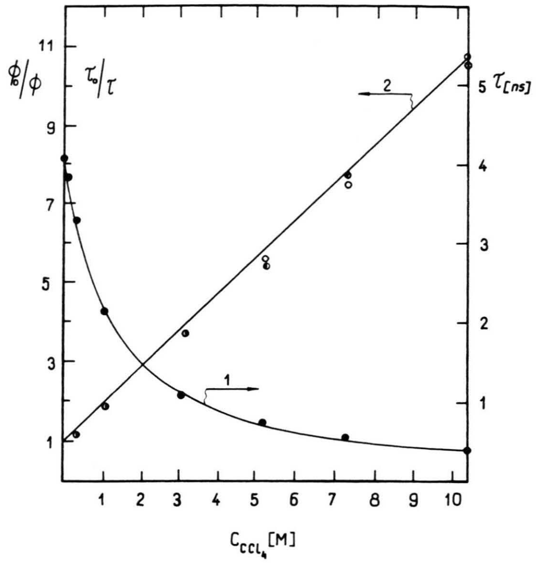


Fig. 3. Fluorescence lifetime of anthracene [1] ($c = 1.6 \times 10^{-4}$ M) and the magnitudes of Φ_0/Φ (-○-○-) and τ_0/τ (-●-●-) [2] as functions of CCl_4 concentrations in the mixtures with cyclohexane.

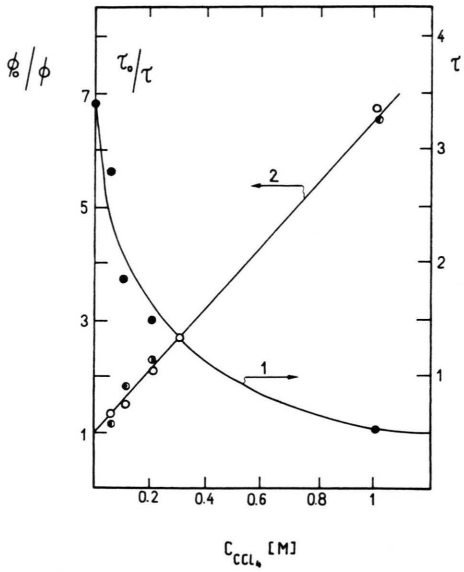


Fig. 4. Fluorescence lifetime of anthracene [1] ($c = 1.6 \times 10^{-4}$ M) and the magnitudes of Φ_0/Φ (-○-○-) and τ_0/τ (-●-●-) [2] as functions of CCl_4 concentrations in the mixtures with benzene.

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

By utilizing the ratio of the quantum yields of fluorescence of anthracene, Φ_0/Φ, 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:

$$(\Phi_0/\Phi)' = 1 + K'_{SV}[CCl_4]_e ,$$

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, Φ_0/Φ, and the quenching by non-bonded CCl_4, $(\Phi_0/\Phi)'$, gives the contribution of the $C_6H_{6-x}(CH_3)_x \cdot CCl_4$ ($x = 0, 2, 3$) complex to the fluorescence quenching of anthracene, $(\Phi_0/\Phi)''$ (Figure 5). In Fig. 6, $(\Phi_0/\Phi)''$ is

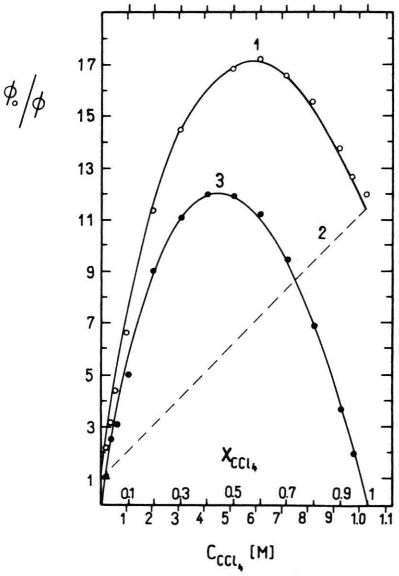


Fig. 5. Relationship between the Φ_0/Φ ratio of the fluorescence of anthracene ($c = 1.6 \times 10^{-4}$ M) in benzene and the CCl_4 concentration [1], CCl_4 non-bonded into a complex with benzene [2] and concentration of the $C_6H_6 \cdot CCl_4$ complex [3].

Table 1. The Stern-Vollmer constants and the rate constants of the fluorescence quenching of anthracene by the non-bonded and bonded CCl_4 in various solvents.

Medium[a]	Non-bonded CCl_4		$C_6H_{6-x}/CH_3/\cdot CCl_4$ complex	
	K'_{SV} (M^{-1})	$k'_q \times 10^{-9}$ ($M^{-1}\,s^{-1}$)	K''_{SV} (M^{-1})	$k''_q \times 10^{-9}$ ($M^{-1}\,s^{-1}$)
Cyclohexane	0.91 ± 0.01	0.224	–	–
Benzene	1.01 ± 0.01	0.269	9.78 ± 0.22	2.87
p-Xylene	0.95 ± 0.01	0.279[b]	6.42 ± 0.09	1.88[b]
Mesitylene	0.84 ± 0.01	0.261[b]	4.22 ± 0.04	1.24[b]

[a] The solutions were not deaerated prior to measurements.
[b] Calculated by assuming the fluorescence lifetime τ_0 as for benzene.

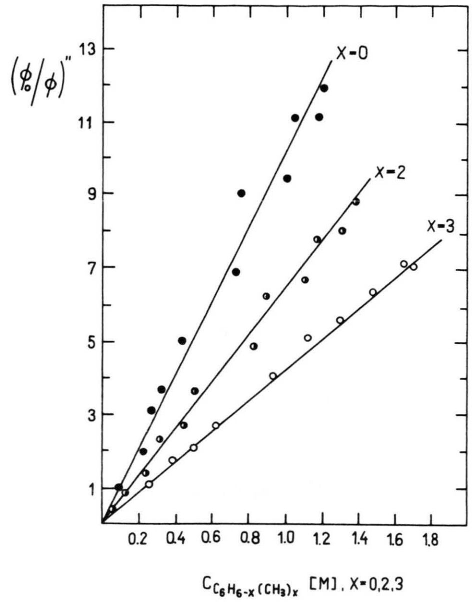


Fig. 6. Fluorescence quenching of anthracene by the $C_6H_{6-x}/CH_3/_x \cdot CCl_4$ ($x = 0, 2, 3$) complexes.

plotted against the concentration of the CCl_4 complex with benzene or methylbenzene. The linearity of the dependence confirms the validity of the model.

In Table 1 the Stern-Volmer constants and the rate constants of the fluorescence quenching of anthracene by the non-bonded and bonded CCl_4 in various solvents are shown.

Remarkable is the poorer efficiency of the fluorescence quenching of anthracene by the more stable CCl_4 complexes with p-xylene or mesitylene as compared to that with benzene. This may have steric reasons.

The rate constants of the fluorescence calculated from the expression $k_f = \Phi \cdot \tau^{-1}$, and the rate constants of the non-radiative deactivation of anthracene, $k_{nr} = (1 - \Phi)\,\tau^{-1}$, in two-component mixtures of tetrachloromethane with cyclohexane and benzene are listed in Table 2.

Table 2. Rate constants of fluorescence and of non-radiative transitions of anthracene in two-component mixtures of CCl_4 with cyclohexane and benzene.

CCl_4 (M)	Cyclohexane		Benzene	
	$k_f \times 10^{-7}$ (s^{-1})	$k_{nr} \times 10^{-7}$ (s^{-1})	$k_f \times 10^{-7}$ (s^{-1})	$k_{nr} \times 10^{-7}$ (s^{-1})
0.00	5.7	19.0	6.2	23.2
0.05	5.7	19.6	5.8	30.0
0.10	5.6	20.3	7.4	46.4
0.21	–	–	6.6	61.0
0.31	5.5	24.6	6.1	71.4
1.03	5.6	40.9	6.0	186.4
3.09	5.6	80.7	–	–
5.15	5.6	131.4	–	–
7.27	6.0	186.3	–	–
10.29	5.8	257.4	5.8	257.4

The data of Table 2 clearly indicate that the fluorescence quenching by tetrachloromethane does not affect the rate constant of fluorescence; affected is the k_{nr} constant, which is the sum of the internal conversion (IC), intersystem crossing (ISC), and of quenching by both the non-bonded and bonded tetrachloromethane:

$$k_{nr} = k^0_{nr} + k'_q\,[CCl_4]_e + k''_q\,[C_6H_{6-x}/CH_3/_x \cdot CCl_4]\,,$$

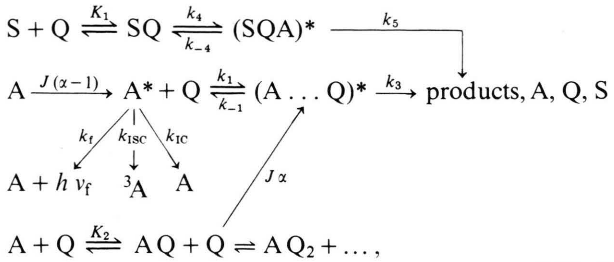
where $k^0_{nr} = k_{IC} + k_{ISC}$.

Having the rate constants k'_q and k''_q, one can compute the contribution of k^0_{nr} to k_{nr}. It amounts approximately to $1.9 \times 10^8\,s^{-1}$ and $2.8 \times 10^8\,s^{-1}$ for cyclohexane and benzene, respectively, k^0_{nr} being independent on the CCl_4 concentration in the mixture thus revealing that CCl_4 does not sensibilize

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 $k''_q = 1.95 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ 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:



where A is the hydrocarbon, Q the quencher and S the solvent. For this scheme, the Φ_0/Φ ratio is determined by the equation

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

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

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

and $[\text{SQ}]_e$ 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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