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

III. Photochemical Interaction of Excited Polycyclic Aromatic Hydrocarbons with Tetrachloromethane in Two-Component Mixtures

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In the photoreactions of polycyclic aromatic hydrocarbons with tetrachloromethane in binary mixtures of tetrachloromethane with cyclohexane, benzene and acetonitrile, both the quenching of the fluorescence and the photoreactions run through an intermediate stage which is an exciplex of the excited hydrocarbon with tetrachloromethane. Abnormal quantum yields of the hydrocarbon decrease are interpreted in terms of the appearance of a new reaction channel *via* a triplex consisting of the excited hydrocarbon, solvent and tetrachloromethane. The photoreaction is quenched by diphenylpicrylhydrazyl, thus suggesting the radical nature of the chemical transformations. A kinetic scheme is suggested for the photophysical and photochemical processes describing the observed phenomena.

1. Introduction

Fluorescence quenching of aromatic hydrocarbons by halomethanes is known to be accompanied by photochemical reactions. Several such systems have been investigated. We refer to the photochemical reactions of benzene and its methyl derivatives with dichloromethane [1] as well as with chloroform and tetrachloromethane [2], the gas-phase photolysis of mixtures of chloroform and benzene [3, 4], and the photochemical reaction of naphthalene with CCl_4 [5].

The most carefully studied reaction was the photochemical addition of tetrachloromethane to anthracene. Bowen and Rohatgi identified its products and suggested the mechanism of this reaction [6, 7]. Transient products of the photoreaction of anthracene and its methyl derivatives with halomethanes and haloethanes were studied by Fogarty and Warner [8] as well as by Vermeerch and coworkers [9]. Selvarajan and associates [10] and Vermeerch et al. [9] demonstrated the free radical nature of this reaction, and that it starts from the first singlet excited state of the hydrocarbon.

Products of the photoreaction of pyrene and perylene with tetrachloromethane were studied by Wiczk and Latowski [11].

Apart from the products, also quantum yields of the decrease of hydrocarbons were determined in photoreactions with halomethanes [6, 12, 13]. The effect of polarity and viscosity of the medium on the photoreaction of anthracene and CCl_4 was studied by Selvarajan et al. [10]. These data, together with knowledge of the effect of solvents on the fluorescence quenching of anthracene by tetrachloromethane enabled the authors of the last-named paper to suggest a detailed mechanism of photoaddition of CCl_4 to anthracene. An intermediate stage of this reaction was a hydrocarbon-tetrachloromethane exciplex. The reaction course *via* the exciplex for reactions of perylene and benzopyrene with CCl_4 was detected by Encinas et al. [13]. Such a reaction mechanism had been advanced earlier by Bowen and Metcalf [14] as well as by Lewis and Ware [15] on the basis of the results of fluorimetric measurements.

2. Experimental

The quantum yields of the decrease of hydrocarbons were measured by irradiation of de-aerated solu-

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tions with a high-pressure mercury burner HBO-200. The exciting radiation (365, 335 and 436 nm for anthracene, pyrene and perylene, respectively) was isolated by glass and liquid filters and its intensity determined with a Hatchard-Parker actinometer [16, 17]. The concentration of the hydrocarbons was determined spectrophotometrically after preliminary determination of the molar absorptivities of each set of solvents. The measurements were run at a wavelength corresponding to the absorption maximum. The irradiation time did not exceed a 10 per cent limit of the progress of the reaction. Variations in the absorbance of the 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical were determined at the maximum of the long wavelength band (515–520 nm).

The fluorimetric measurements were run on a modular spectrofluorimeter according to [18]. The hydrocarbons were purified by column chromatography. DPPH (BDH Chemical Ltd.) and the spectrograde solvents were used as received.

3. Results

The observed quantum yields of the aromatic hydrocarbons vs. the tetrachloromethane concentration in the binary mixtures with benzene, cyclohexane and acetonitrile are shown in Figures 1–3. In the tetrachloromethane–acetonitrile mixtures, the quantum yields first increase rapidly with increasing CCl_4 concentration, and after attaining a maximum at about 1 M CCl_4 fall off, reaching the following values in pure CCl_4:

0.421 ± 0.015	for anthracene,
0.193 ± 0.070	for pyrene,
0.084 ± 0.002	for perylene.

In the tetrachloromethane–benzene mixtures the initial quantum yields increase not as rapidly (with the exception of anthracene), and peak values are attained at higher CCl_4 concentrations (about 5 M).

In the tetrachloromethane–cyclohexane mixtures the initial rise is even more slowly, and the highest quantum yields are attained in pure CCl_4. The nature of the hydrocarbon has no influence on the shape of the curves. Only the maximum values of the quantum yields change.

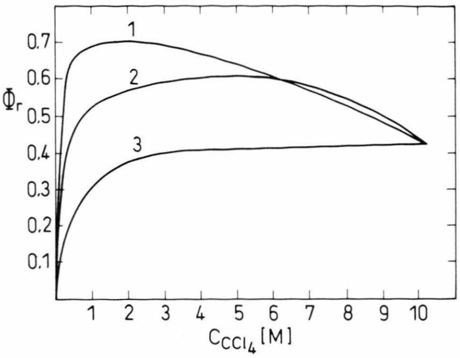

Fig. 1. Quantum yield of the decrease of anthracene ($c = 6.4 \cdot 10^{-4}$ M) vs. CCl_4 concentration in mixtures with acetonitrile (1), benzene (2) and cyclohexane (3).

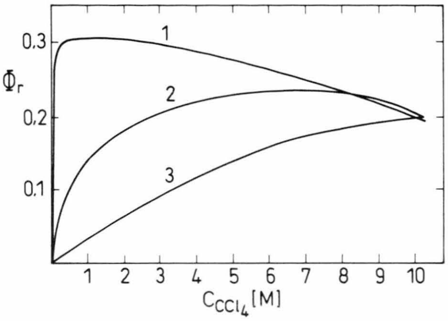

Fig. 2. Quantum yield of the decrease of pyrene ($c = 1.0 \cdot 10^{-4}$ M) vs. CCl_4 concentration in mixtures with acetonitrile (1), benzene (2) and cyclohexane (3).

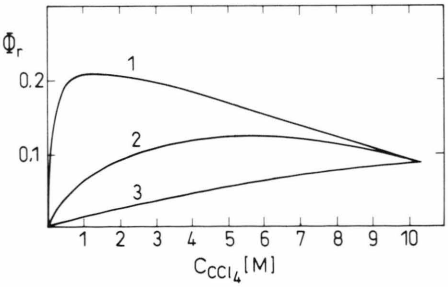

Fig. 3. Quantum yield of the decrease of perylene ($c = 3.0 \cdot 10^{-5}$ M) vs. CCl_4 concentration in mixtures with acetonitrile (1), benzene (2) and cyclohexane (3).

In de-aerated solutions, anthracene undergoes photodimerization upon irradiation with the 365 nm line. The quantum yields of the decrease of anthracene ($c = 6.4 \cdot 10^{-4}$ M) in acetonitrile, benzene and cyclohexane are 0.037, 0.020 and 0.015, respectively. They match those of the photodimerization of anthracene at the $1.0 \cdot 10^{-3}$ M concentration in benzene, which amounts to 0.0192 ± 0.0052 [19].

Irradiation of pyrene ($c = 1.0 \cdot 10^{-4}$ M) and perylene ($c = 5.0 \cdot 10^{-5}$ M) in these solvents does not produce,

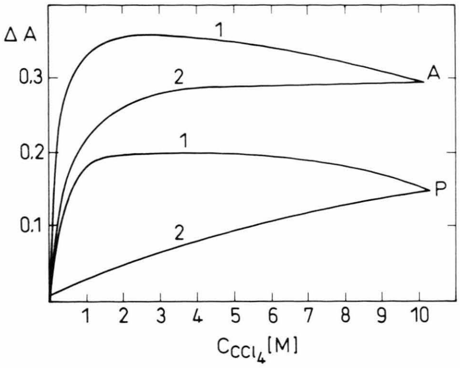

Fig. 4. Absorbance variation of the DPPH radical (ΔA) on irradiation of anthracene (A) and perylene (P) in binary mixtures of CCl_4 with benzene (1) and cyclohexane (2) vs. CCl_4 concentration.

with the exception of pyrene/CH_3CN, measurable variations in concentration of these hydrocarbons. The quantum yield of the decrease of pyrene in acetonitrile is 0.009 ± 0.002. The quantum yields of the decrease of anthracene in 0.05 M CCl_4 solutions in acetonitrile, benzene and cyclohexane are comparable with those reported by Selvarajan and associates for 0.04 M CCl_4 solutions in these solvents [10].

Addition of bromobenzene to anthracene in a mixture of CCl_4 with benzene suppresses the quantum yields of both the photoreaction of anthracene with tetrachloromethane and of the fluorescence of the hydrocarbon [20]. At a fixed CCl_4 concentration the magnitude of these variations depends on the concentration of the bromine added and obeys the Stern-Volmer equation. The slopes of the straight lines illustrating the quenching of both the reaction and the fluorescence of anthracene by bromobenzene in the binary mixtures of CCl_4 with benzene, cyclohexane and acetonitrile are given in Table 1.

Table 1. Slopes of the straight lines of quenching of the reaction and of the fluorescence of anthracene ($c = 6.4 \cdot 10^{-4}$ M) by bromobenzene in binary mixtures of CCl_4 with benzene, cyclohexane and acetonitrile (CCl_4 concentration 0.13 M).

Solvent	Quenching of	
	reaction	fluorescence
Benzene	0.777 ± 0.003 0.68 ± 0.02 [a]	0.743 ± 0.010 0.72 ± 0.06 [a]
Cyclohexane	1.356 ± 0.077	1.346 ± 0.051
Acetonitrile	0.400 ± 0.022	0.351 ± 0.011

[a] taken from [20].

It has been pointed out in many reports [9, 10, 21–25] that the fluorescence quenching of aromatic hydrocarbons by halomethanes is accompanied by the generation of free radicals. The presence of both chloroform and hexachloroethane among the photoreaction products reveals the free-radical nature of the reaction [6, 9–11].

The free-radical mechanism is supported by measurements of the absorption of the DPPH radical. Figure 4 shows absorbance variations of the DPPH radical on irradiation of anthracene and perylene in binary mixtures of CCl_4 with cyclohexane and benzene vs. CCl_4 concentration. The curves resemble the quantum yield curves of the decrease of these hydrocarbons (Figs. 1 and 3).

4. Discussion

The dependence of the quantum yield ϕ_r of the decrease of the hydrocarbons on the CCl_4 concentration can be related to the quenching of the hydrocarbons by CCl_4. The more efficient fluorescence quenching corresponds to the higher quantum yield of the hydrocarbon decrease. "Parabolic" curves of the fluorescence quenching are paralleled by quantum yield curves of the decrease of hydrocarbons exhibiting a maximum (for mixtures of CCl_4 with C_6H_6 and CH_3CN). The relationship $\phi_r = f(CCl_4)$ for the C_6H_{12}–CCl_4 mixture is normal. The quenching of fluorescence for this mixture can be described by the Stern-Volmer equation. These findings can be illustrated by plotting ϕ_r/ϕ_{max} vs. ϕ/ϕ_0 (Fig. 5) for anthracene and CCl_4 concentrations in binary mixtures with C_6H_6, C_6H_{12} and CH_3CN. Some differences in the shapes of the curves can be attributed to the involvement of the hydrocarbon not only in the primary photochemical reaction but also in "dark" reactions.

The correlation between the quantum yield of fluorescence and that of the photochemical reaction supports a mechanism, postulated by different authors, involving participation of the hydrocarbon in its first singlet excited state in the photochemical reaction [6, 10, 13–15]. Bromobenzene quenches the fluorescence of anthracene, thus raising the efficiency of intersystem transition [26]. The similarity of the slopes of the fluorescence quenching and of the reaction of anthracene by bromobenzene in all the mixtures confirms the suggestion that the photoaddition

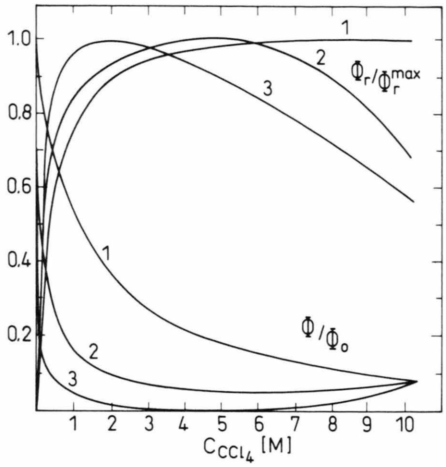

Fig. 5. Relationship ϕ_r/ϕ_r^{max} of the reaction and ϕ/ϕ_0 of the fluorescence for anthracene in binary mixtures of CCl_4 with cyclohexane (1), benzene (2) and acetonitrile (3) vs. CCl_4 concentration.

of CCl_4 to anthracene starts from the excited singlet state of the hydrocarbon [20, 29].

The start of the reaction from the S_1 state of the hydrocarbons enables the explanation of the relationship between the quantum yield of hydrocarbon decrease and CCl_4 concentration on the basis of the fluorescence quenching curves. The dependence of the quantum yield of the decrease and that of fluorescence of the hydrocarbons on quencher concentration in the C_6H_{12}–CCl_4 mixture is normal. On the other hand, these two relationships for the remaining mixtures (CH_3CN–CCl_4 and C_6H_6–CCl_4) have a non-typical "parabolic" shape.

The parabolic shape of the fluorescence quenching curves by CCl_4 observed for a variety of polycyclic aromatic hydrocarbons in binary mixtures of tetrachloromethane with different solvents can be explained by assuming that the fluorescence quencher in these mixtures may be the "free", uncomplexed CCl_4 and its complex with the other component of the mixture [28, 29]. In the case of formation by the quencher of a more efficiently quenching complex with the component, the observed "parabolic" shape of the quenching curve is due to the type of relationship between the complex being formed and the CCl_4 concentration in a particular binary mixture [28]. The higher rate constants of fluorescence quenching of anthracene and the higher quantum yields of the decrease of the hydrocarbon in benzene as compared to those in cyclohexane, both at lower quencher concentrations [10] and over the whole accessible range of its concentrations in mixtures with various "inert" solvents [28, 29] were explained in terms of the presence of weak complexes formed by π-p interaction of benzene with tetrachloromethane.

Fluorescence quenching of anthracene and other aromatic hydrocarbons by CCl_4 depends strongly on the medium polarity. For instance, the rate constant of the fluorescence quenching is higher in methanol than in hexane. This confirms the participation of the exciplex in fluorescence quenching [10, 13–15, 29]. In many solvents, whose electric permeabilities differ from that of CCl_4, it acts not only as the fluorescence quencher but also as a constituent lowering the medium polarity, thus leading to reduced efficiency of fluorescence quenching [29]. This is particularly evident at high quencher concentrations. A similar effect of the quencher on medium polarity, and hence on the quenching efficiency, was reported by Murata, who studied the fluorescence quenching of 2-ethoxynaphthalene by methyl benzoate in dimethylformamide [30]. In such mixtures, "parabolic" quenching curves are the outcome of the contribution, apart from the "free" quencher, of a solvent-quencher complex as well as lowering of the medium polarity with increasing CCl_4 concentration in the two-component mixture. The mutual contribution of these two mechanisms to the fluorescence quenching may vary for different solvents.

Both the presented results and the literature evidence enable to suggest the following kinetic scheme of photophysical and photochemical processes:

$$S+Q \overset{K_1}{\rightleftharpoons} SQ,$$

$$A+Q \overset{K_2}{\rightleftharpoons} AQ+Q \rightleftharpoons AQ_2+\ldots,$$

$$A \xrightarrow{J(1-\alpha)} A^*$$

$$A^* \xrightarrow{k_f} A+h\nu_f, \qquad A^* \xrightarrow{k_{ic}} A, \qquad A^* \xrightarrow{k_{isc}} {}^3A$$

$$\begin{tikzcd}
AQ \arrow[d, "\alpha J"] & & A, Q \\
A^*+Q \arrow[r, shift left, "k_1"] & (AQ)^* \arrow[l, shift left, "k_{-1}"] \arrow[ur, "k_2"] \arrow[r, "k_3"] & \text{products} \\
A^*+SQ \arrow[r, shift left, "k_4"] & (ASQ)^* \arrow[l, shift left, "k_{-4}"] \arrow[ur, "k_5"] \arrow[r, "k_6"] & A, S, Q,
\end{tikzcd}$$

where A, Q, and S stand for the hydrocarbon, the quencher and the solvent respectively.

The shape of the quenching curves for such a scheme can be described by

$$\frac{\phi_0}{\phi} = \frac{1+k_1[\mathrm{Q}]_\mathrm{e}\,\tau_0\,p + k_4[\mathrm{SQ}]_\mathrm{e}\,\tau_0\,p'}{1-\alpha p}, \tag{1}$$

where τ_0 is the fluorescence lifetime of the hydrocarbon in the abscence of quencher,

$$\tau_0 = (k_\mathrm{f} + k_\mathrm{ic} + k_\mathrm{isc})^{-1}.$$

$$p = \frac{k_2+k_3}{k_{-1}+k_2+k_3} \quad \text{and} \quad p' = \frac{k_5+k_6}{k_{-4}+k_5+k_6}$$

determine the degree of decay of particular species, α determines the fraction of the exciting radiation absorbed by the complex AQ,

$$\alpha^{-1} = 1 + \left(\frac{\varepsilon_\mathrm{A}}{\varepsilon_\mathrm{AQ}}\right)\cdot\left(\frac{1}{K_2[\mathrm{Q}]_\mathrm{e}}\right). \tag{2}$$

[SQ] is the concentration of the solvent-quencher complex, and the index e denotes equilibrium concentration.

The equation describing the dependence of the quantum yield of decrease of the hydrocarbon, developed on the basis of the adopted scheme of the processes, is an implicit function of the quencher concentration. For the CCl_4-cyclohexane mixtures both the quenching of fluorescence as well as the progress of the reaction *via* the solvent-quencher complex can be omitted in the scheme, thus simplifying the equation describing the dependence of quantum yield of the decrease of hydrocarbon on quencher concentration:

$$\phi_\mathrm{r} = \frac{k_3\,\tau_\mathrm{exc}(k_1[\mathrm{Q}]\,\tau_0 + \alpha)}{1+k_1[\mathrm{Q}]\,\tau_0\,p}, \tag{3}$$

where τ_exc is the lifetime of the exciplex (AQ)*.

The reciprocal of this relationship can be written as

$$\frac{1}{\phi_\mathrm{r}} = \frac{1}{k_3\,\tau_\mathrm{exc}(k_1[\mathrm{Q}]\,\tau_0+\alpha)} + \frac{k_1[\mathrm{Q}]\,\tau_0\,p}{k_3\,\tau_\mathrm{exc}(k_1[\mathrm{Q}]\,\tau_0+\alpha)}. \tag{4}$$

The measurements of the fluorescence quenching of anthracene by CCl_4 in cyclohexane have shown that during excitation with the 365 nm line the contribution of static quenching at not too low concentrations is negligible, i.e. $\alpha \simeq 0$ [15, 28]. Hence, ignoring α in (4), we obtain

$$\frac{1}{\phi_r} = \frac{1}{k_3 k_1[\mathrm{Q}]\,\tau_0\,\tau_\mathrm{exc}} + \frac{k_2}{k_3} + 1. \tag{5}$$

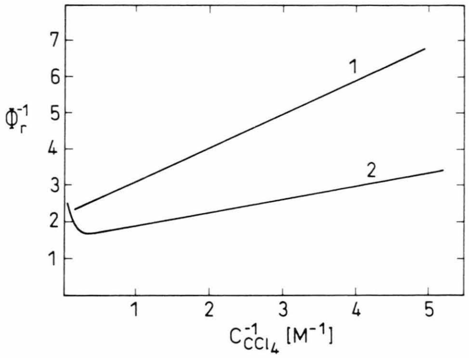

Fig. 6. Relationship between reciprocal quantum yield of the decrease of anthracene on reciprocal quencher concentration in cyclohexane (1) and benzene (2).

The linear relationship between the reciprocal quantum yield of the decrease of the hydrocarbon on the reciprocal quencher concentration (for anthracene in CCl_4-cyclohexane mixtures; Fig. 6) supports the correctness of the adopted model. The k_2/k_3 ratio calculated from this equation for anthracene and pyrene in cyclohexane is 1.30, and for perylene it is 3.7. It must, however, be borne in mind that the equation was derived under the assumption that $\alpha \simeq 0$, this being a too rough approximation for pyrene and perylene [29]. The hydrocarbons considered are involved in "dark" reactions, hence the calculated magnitudes are only proportional to the actual ones.

The hydrocarbon-CCl_4 exciplex being formed does not fluoresce. It is thus impossible to investigate its behaviour directly. It can be assumed, however, that it possesses an ion-pair structure $(\overset{+}{A^{\cdot}} \cdots \overset{-}{CCl_4^{\cdot}})$. In the polar medium the ion-pair can dissociate to produce free radical ions with simultaneous degradation of $CCl_4^{\cdot}$ to more thermodynamically stable fragments, a trichloromethyl radical and a chloride ion. In media of low electric permeability the chloride ion can combine with $\overset{+}{A^{\cdot}}$ to form a neutral radical pair, $ACl^{\cdot} \cdots CCl_3^{\cdot}$. Formation of such a pair may also take place in a polar medium when the ion-pair becomes occluded in a cage of solvent.

Addition of a radical scavenger to the reacting medium, such as DPPH, reduces the quantum yield of the decrease of the hydrocarbon with simultaneous disappearance of the absorption band due to DPPH.

For high quencher concentrations, $[\mathrm{Q}] \to \infty$, (3) becomes

$$\phi_\mathrm{r}^\infty = \frac{k_3\,\tau_\mathrm{exc}}{p}. \tag{6}$$

Relative variations of the absorbance of the DPPH radical and the relative quantum yield of the reaction can be represented as

$$\frac{\Delta A^{\infty}}{\Delta A} - 1 \simeq \frac{\phi_r^{\infty}}{\phi_r} - 1 = \frac{1}{p k_1 [\mathrm{Q}] \tau_0} = \left(\frac{\phi_0}{\phi} - 1 \right)^{-1}. \quad (7)$$

Slopes of the straight lines determined from the measurements of the decay of absorbance of the DPPH radical and of quantum yields of the fluorescence of anthracene and perylene in the CCl_4-cyclohexane mixture are listed in Table 2.

Table 2. Slopes of the straight lines determined from the decay of absorbance of the DPPH radical and quantum yields of the fluorescence in the CCl_4-cyclohexane mixture.

Hydrocarbon	Fluorescence	Radical
Anthracene	0.77	0.84
Perylene	9.32	6.19

One of the reasons for the considerable differences between the coefficients for perylene is overlapping of the DPPH radical absorption with that of the photoproducts of the reaction between perylene and CCl_4 being formed. The agreement of these coefficients provides a further proof in favour of the correctness of the adopted model in which the fluorescence quenching with the formation of the exciplex constitutes an intermittent stage of the photochemical reaction of the radical type. The non-typical shape of the quantum yield of the decrease of the hydrocarbons in mixtures of CCl_4 with benzene and acetonitrile is due to the appearance of a new reaction channel, *via* the hydrocarbon-solvent-quencher triplex.

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