The Effect of Temperature on the Fluorescence Quenching of Perylene by Tetrachloromethane in Mixtures with Cyclohexane and Benzene

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The effect of temperature on the fluorescence quenching of perylene has been studied in a variety of two-component mixtures of CCl_4 with cyclohexane and benzene. Results of these studies are explained in terms of specific interactions between the components of the mixtures.

The fluorescence of polycyclic aromatic hydrocarbons is quenched by halomethanes. The quenching is accompanied by a photochemical reaction [1, 2]. A "weak" non-fluorescent exciplex formed between the excited hydrocarbon and the haloderivative has been postulated as an intermediate in that process. The effect of substituents in the hydrocarbon and the polarity of the solvent on the efficiency of quenching supports this mechanism [3–8].

In the case of the fluorescence quenching of aromatic hydrocarbons by tetrachloromethane it was found that, at high quencher concentrations in solvents other than aliphatic hydrocarbons, the quenching curves had an unusual "parabolic" shape [9–11]. That shape was explained by the assumption that, besides the "free" noncomplexed CCl_4, its complex with another component of the mixture, more effectively quenching the fluorescence, participates in the quenching process. Consequently, the "parabolic shape" of the curve is determined by the dependence of the concentration of the complex being formed on the CCl_4 concentration in the mixture [9].

The temperature has been found to have a significant effect on the efficiency of the fluorescence quenching of anthracene and its derivatives by a variety of halogen compounds, including tetrachloromethane [8, 12]. In this report we demonstrate the influence of temperature on the fluorescence quenching of perylene by tetrachloromethane in benzene and cyclohexane.

Figure 1 shows the ratio of the quantum yields of fluorescence, ϕ_0/ϕ, of perylene vs. quencher concentration at various temperatures in deoxygenated mixtures with benzene and cyclohexane. The shape of the quenching curves does not change markedly with temperature.

In Table 1 the Stern-Volmer constant, K_{SV} (for $[Q] \rightarrow 0$) at various temperatures is listed for the fluorescence quenching of perylene by CCl_4 in benzene and cyclohexane.

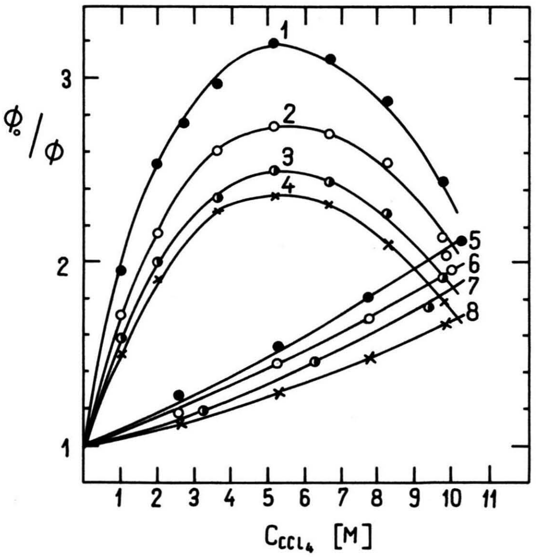

Fig. 1. Fluorescence quenching curves of perylene ($c = 3 \times 10^{-5}$ M) by CCl_4 in benzene at 45 °C (1), 35 °C (2), 22 °C (3), 12.5 °C (4) and in cyclohexane at 45 °C (5), 33 °C (6), 22 °C (7), 13 °C (8).

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Table 1. The Stern-Volmer constants, K_{SV} (for $[Q] \to 0$), of the fluorescence quenching of perylene by CCl_4 in benzene and cyclohexane at various temperatures.

Compound	Benzene		Cyclohexane	
	K_{SV} [$dm^3\ mol^{-1}$]	T [K]	K_{SV} [$dm^3\ mol^{-1}$]	T [K]
Perylene	0.486	285.5	0.038	286
	0.536	295	0.048	295
	0.683	308	0.069	306
	0.990	318	0.100	318

Table 2. Activation energies of the fluorescence quenching of perylene by CCl_4 (0.2 M) in benzene and cyclohexane and viscosity-based energies of activation of these solvents.

Compound	Benzene		Cyclohexane	
	E_a [$kJ\ mol^{-1}$]	E_η [$kJ\ mol^{-1}$]	E_a [$kJ\ mol^{-1}$]	E_η [$kJ\ mol^{-1}$]
Perylene	16.60	9.47	20.16	14.45

Table 3. Activation energies for the fluorescence quenching of perylene by CCl_4 and viscosity-based energies of activation for mixtures of CCl_4 with cyclohexane, benzene and for pure CCl_4.

Mixture	E_a [$kJ\ mol^{-1}$]	E_η [$kJ\ mol^{-1}$]
$C_6H_{12} + 2\ M\ CCl_4$	21.18	13.67
$C_6H_{12} + 6\ M\ CCl_4$	13.56	13.38
CCl_4 only	10.53	10.63
$C_6H_6 + 2\ M\ CCl_4$	12.31	10.28
$C_6H_6 + 6\ M\ CCl_4$	10.33	10.68

Plots of $\ln K_{SV}$ vs. $1/T$ are linear. The calculated values of the activation energy, E_a, are shown in Table 2 together with the viscosity-based energy of activation, E_η, calculated from the temperature dependence of the dynamic viscosity (measured in a Hoeppler viscometer).

The activation energies determined from the process of fluorescence quenching are higher than the viscosity-based ones for both the low concentration of CCl_4 (as used for obtaining the data of Table 2) and the high CCl_4 concentrations in the mixture. Table 3 shows the energies of activation determined from the relationship $\ln(\phi_0/\phi - 1)$ vs. $1/T$ for the mixtures (at fixed CCl_4 concentration in cyclohexane and benzene) and for pure CCl_4.

The data of this Table show that the activation energy, initially higher than the viscosity-based one, falls with increasing CCl_4 concentration and becomes comparable with E_η.

The simpler system for the analysis of the effect of temperature on the quenching efficiency is that with cyclohexane. In this case, the contribution of static quenching can be neglected by assuming that only "free" CCl_4 takes part in the quenching and the expression for ϕ_0/ϕ can be written in the simplified form

$$\phi_0/\phi = 1 + \frac{k_1 k_3}{k_{-1} + k_3} \tau_0 [Q] . \qquad (1)$$

Further, assuming after Lewis and Ware [13] that $k_3 < k_{-1}$ and $\Delta E_1 \simeq \Delta E_{-1}$ (encounter complex), the measured energy of activation is $E_a = E_3 - E_\phi$. The obtained E_3 value of 13.9 kJ/mol is comparable with the viscosity-based activation energy.

The ϕ_0/ϕ ratio of the quantum yield of fluorescence, describing the "parabolic" quenching curves, is an implicit function of temperature. Temperature-dependent are all rate constants of formation and dissociation into substrate and photoproducts of the hydrocarbon-CCl_4 exciplex and hydrocarbon-CCl_4-benzene triplex. Temperature-dependent are also the equilibrium concentrations of the quencher and its complex with the solvent and with a polycyclic hydrocarbon in the ground state. This makes it highly difficult to analyse the effect of temperature on the fluorescence quenching in this system.

In the CCl_4-benzene mixtures an increase in the temperature brings about dissociation of weak complexes which strongly quench the fluorescence. This would result in flattening of the quenching curves with increasing temperature. Such a flattening in the curve of fluorescence quenching by CCl_4 is not observed for perylene dissolved in benzene.

The benzene-CCl_4 complex belongs to the class of weak complexes. The enthalpy of its formation is −5.28 kJ/mol at 298 K [14], and this value is comparable with known, not too high values of the enthalpy of formation of other CCl_4 weak complexes with: toluene (−4.35 kJ/mol) [14] and p-xylene (ca. −4 kJ/mol) [14, 15]. The range of temperatures applied during the experiments was rather narrow because of the low boiling point of the solvents and the high freezing point of benzene. Though the small temperature changes were sufficient to facilitate the formation of non-fluorizing exciplexes due to viscosity changes, and to accelerate the complex dissociation, the changes were probably too small to enhance the dissociation of benzene-CCl_4 complexes so effectively that some flattening in the fluorescence quenching curves might be observed.

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