The Effect of Oxygen on the Fluorescence Quenching of Polycyclic Aromatic Hydrocarbons in Two-Component Mixtures of CCl_4 with Cyclohexane, Benzene, and Acetonitrile

Andrzej Chojnowski and Wiesław M. Wiczk
Institute of Chemistry, University of Gdańsk, 80-952 Gdańsk, Poland

Tadeusz Latowski
Institute of Chemistry, Pedagogical University, 25-020 Kielce, Poland

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Fluorescence quenching of anthracene and perylene has been studied in deoxygenated and non-deoxygenated two-component mixtures of CCl_4 with cyclohexane, benzene and acetonitrile. It was indicate that the dissolved oxygen only reduces the fluorescence lifetimes of the hydrocarbons, thus suppressing the efficiency of quenching.

The fluorescence quenching of polycyclic aromatic hydrocarbons by halomethanes and accompanying photochemical reactions have been studied since some years. The influence of the medium and of substituents in the molecules of these hydrocarbons suggest a quenching mechanism involving charge or electron transfer [1–8]. An exciplex formed between the excited hydrocarbon molecule and the haloderivative in its ground state does not fluoresce. Over the range of high quencher (CCl_4) concentrations the fluorescence quenching curves of polycyclic aromatic hydrocarbons have unusual shapes. With the exception of inert solvents, such as aliphatic hydrocarbons, the quenching curves are "parabolic" [6–8] owing to participation of the "free" uncomplexed quencher of its complex with the solvent in the quenching process. In the case of formation by the quencher of a more effectively quenching complex with a component of the mixture, the "parabolic shape" of the quenching curve depends on the relationship between the concentration of the complex being formed and the CCl_4 concentration in a particular binary mixture. In polar media also the decrease in electric permeability of the medium with increasing CCl_4 concentration [7, 8] contributes to the reduction of quenching.

The measurements of the quenching were run in deoxygenated solutions in which the dissolved oxygen was removed by passing a stream of nitrogen through the solution immediately before the measurement. The presence of oxygen in solution reduces the lifetime of the hydrocarbon in the excited state thus resulting in lowering the quantum yield of fluorescence (Tables 1 and 2).

Figure 1 shows examples of the fluorescence quenching curves of anthracene by CCl_4 in deoxygenated and non-deoxygenated two-component mixtures with cyclohexane and benzene. Oxygen in solution does not affect the qualitative composition of the systems.

In non-deoxygenated mixtures the maxima are lower than in the deoxygenated ones. For anthracene and perylene, in binary mixtures of CCl_4 with cyclohexane, benzene and acetonitrile, the ratio of the quantum yields in the deoxygenated and non-deoxygenated mixture,

$$\frac{(\phi_0/\phi)_{\text{deoxyg.}}}{(\phi_0/\varphi)_{\text{non-deoxyg.}}},$$

is, within the range of experimental error, equal to values listed in Table 3 for pure solvents and is independent of the CCl_4 concentration. This means that the dissolved oxygen affects the lifetime of neither the hydrocarbon-CCl_4 exciplex nor the hydrocarbon-solvent-CCl_4 triplex, but it only reduces the fluorescence

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Reprint requests to Dr. T. Latowski, Institute of Chemistry, Pedagogical University, 25-020 Kielce, Poland.

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Table 1. Lifetimes (in ns) and quantum yields of the fluorescence of anthracene ($c = 6.4 \times 10^{-4}$ M) in deoxygenated and non-deoxygenated solvents.

Solvent	$\phi_{\text{non-deoxyg.}}$		$\phi_{\text{deoxyg.}}$		$\tau_{\text{non-deoxyg.}}$		$\tau_{\text{deoxyg.}}$
	Literatur	Measured	Literatur	Measured	Literatur	Measured	Literatur
Cyclohexane	–	0.23	0.30 [b]	0.28	3.8 [c] 3.97–4.10 [d]	4.06	4.9 [b] 6.8–5.03 [d]
Benzene	0.19 [a]	0.21	0.26 [b]	0.25	–	3.41	4.1 [b] 3.6–4.0 [d]
Acetonitrile	–	0.16	–	0.23	–	4.54	5.0 [e]
Tetrachloromethane	0.02 [a]	0.022	–	0.021	–	0.52	–

[a] Taken from [9], [b] [10], [c] [11], [d] [12], [e] [13].

Table 2. Lifetimes (in ns) and quantum yields of the fluorescence of perylene ($c = 3 \times 10^{-5}$ M) in deoxygenated and non-deoxygenated solvents.

Solvent	$\phi_{\text{nondeoxyg.}}$	$\phi_{\text{deoxyg.}}$		$\phi_{\text{nondeoxyg.}}$	$\phi_{\text{deoxyg.}}$
	Meas.	Lit.	Meas.	Meas.	Lit.
Cyclohexane	0.756	0.94 [a] 0.78 [b] 0.98 [d]	0.94	5.27 ±0.10	6.4 [b]
Benzene	0.760	0.89 [b]	0.89	5.02 ±0.08	4.79 –6.9 [b]
Acetonitrile	0.680	–	0.87	4.21 ±0.10	4.8 [c]
Tetrachloromethane	0.410	–	–	3.01 ±0.07	–

[a] Taken from [14], [b] [10], [c] [13], [d] [15].

Table 3. The ratio of the quantum yields of fluorescence, ϕ/ϕ_0, of anthracene and perylene in cyclohexane, benzene and acetonitrile.

Compound	ϕ/ϕ_0			
	Cyclohexane		Benzene	Acetonitrile
	Lit.	Meas.	Meas.	Meas.
Anthracene	1.25 [a] 1.30 [b]	1.22	1.20	1.43
Perylene	1.30 [a] 1.28 [c]	1.24	1.17	1.28

[a] Taken from [14], [b] [11] (from measurements of time of fluorescence decay), [c] [16].

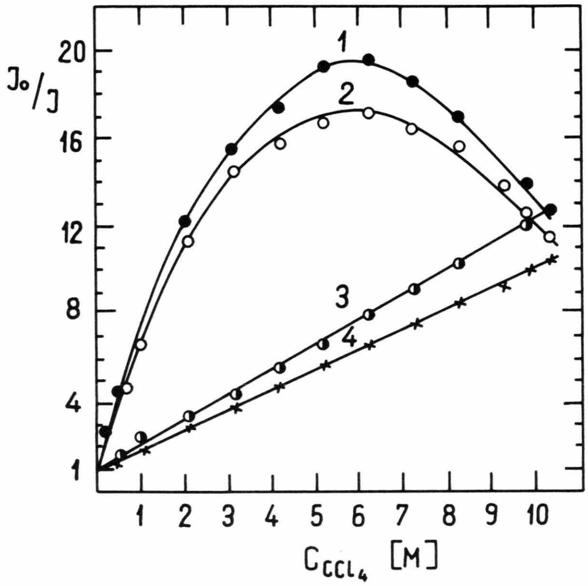

Fig. 1. Fluorescence quenching curves of anthracene ($c = 1.6 \times 10^{-4}$ M) by CCl_4 in deoxygenated (1) and non-deoxygenated (2) benzene and in deoxygenated (3) and non-deoxygenated (4) cyclohexane.

lifetimes of the hydrocarbons, thus suppressing the efficiency of quenching. Consequently, the lifetime of the exciplex should be shorter than the lifetime of the excited hydrocarbon. This conclusion complies with the lifetime of the 9,10-dichloroanthracene-CCl_4 exciplex estimated to ca. 5×10^{-12} s by Ware and Lewis [2].

[1] E. J. Bowen and W. S. Matcalf, Proc. Roy. Soc. London **A 206,** 437 (1951).
[2] W. R. Ware and C. Lewis, J. Chem. Phys. **57,** 3546 (1972).
[3] M. V. Encinas, M. A. Rubio, E. A. Lissi, J. Photochem. **18,** 137 (1982).
[4] D. Schulte-Frohlinde and R. Pfefferkorn, Ber. Bunsenges. Phys. Chem. **72,** 330 (1968).
[5] E. J. Bowen and J. Sahn, J. Phys. Chem. **63,** 4 (1959).
[6] W. M. Wiczk and T. Latowski, Z. Naturforsch. **41 a,** 761 (1986).
[7] W. M. Wiczk and T. Latowski, Z. Naturforsch. **42 a,** 1290 (1987).
[8] W. M. Wiczk and T. Latowski, Z. Naturforsch. **46 a,** 259 (1991).

[9] E. J. Bowen and G. Norton, Trans. Faraday Soc. **35,** 44 (1939).
[10] J. B. Birks, Photophysis of Aromatic Molecules, John Wiley Interscience, New York 1970, p. 127.
[11] L. K. Patterson, G. Porter, and M. R. Topp, Chem. Phys. Lett. **7,** 612 (1970).
[12] R. A. Lampert, L. A. Chewter, D. Phillips, D. V. O'Connor, A. J. Roberts, and S. R. Meech, Anal. Chem. **55,** 68 (1983).
[13] A. R. Watkins, Chem. Phys. Lett. **65,** 380 (1979).
[14] J. B. Berlman, Handbook of Fluorescence Spectra of Aromatic Molecules, Academic Press, New York 1965.
[15] C. A. Parker and T. A. Joyce, Chem. Comm. **1969,** 108.
[16] C. S. Parmenter and J. D. Ran, J. Chem. Phys. **51,** 2242 (1969).